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CSMCRI technologies for water desalination and pollution control

B D Dasare & A V Rao

Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002

Received 14 September 1993

The CSMCRI has been working on treatment of effluents of some important industries like fertilizer, oil refinery, paper and pulp and chlor-alkali. This paper presents in brief laboratory and developmental work carried out at the Institute on water desalination and pollution control.

Environmental pollution has reached an alarming proportion due to rapid population growth, increasing urbanization and industrial development. Of all the environmental resources, water is severely threatened by pollution and water pollution control has been given a high priority in many countries. The pollution may be of organic or inorganic in nature. The heavy metal ions in water as a result of industrial effluent discharge are one of the worst inorganic pollutants and have caused disasters in many a times in many countries. The organic pollutants thrown out by industries have caused concern in all quarters. The need to remove such pollutants from water has added a new dimension to waste water treatments and it has now become necessary to search for techno-economically viable methods for the removal of such obnoxious constituents from waste water so that the effluents of industries are safely discharged or reused after further suitable treatments.

In a major thrust on desalination of brackish water, CSMCRI has developed desalination technology of reverse osmosis and electrodialysis and others such as polymeric adsorbents/ion-exchange resins in the field of industrial effluent treatment. In order to transfer these technologies to actual practice on large scale, utility-cum-demonstration plants of varying capacities are designed, fabricated, installed and commissioned in several places in Gujarat, Rajasthan and Tamil Nadu for producing potable water from brackish water. Such projects are supported by the Ministry of Works & Housing, Govt. of India and Public Health Engineering Departments of Govt. of Gujarat and Tamil Nadu. Although these technologies are developed primarily for the purpose of the desalination of water, they have got many spin-off potential applications in industrial fluid processing such as separation, concentration and recovery of many innocuous or deleterious constituents and are thus ideal to solve

certain water pollution problems. The CSMCRI has made a preliminary survey and located such pollution problems which cannot be treated by the conventionally established water pollution control methods. Such water pollution problems emanate from fertilizer industry, chlor-alkali industry, textile industry, refineries, pulp and paper industry, dairy industry, etc.

(i) Ammonia removal from the waste water of fertilizer industry

Nitrogenous compounds have been recognised as water pollutants and the deleterious effects of their presence in waste waters are felt in the form of depletion of oxygen in such water, toxicity to human and aquatic life and the putrefaction of the receiving streams. Among the various sources that contribute nitrogenous compounds to the surface waters, fertilizer industries play a major role. Rigid specifications have been laid down for the concentration of various constituents in the waste water of the fertilizer industries' effluent. The composition and the volume of the waste water of the fertilizer industry varies over a wide range depending on the technology adopted, process variations resorted to and the operating philosophies followed in the housekeeping. Among the nitrogenous compounds in the waste water of fertilizer industry, ammonia is the most prominent pollutant.

Of the various methods tried for removal of ammonia from waste water, ion-exchange technique has been extensively studied in this Institute. Conventional gel type weakly acidic cation exchanger creates a lot of operational problems due to abnormal swelling when converted from H^+ form to NH_4^+ form. A weakly acidic porous cation exchanger based on methacrylic acid is developed which shows very less swelling when converted to NH_4^+ form as compared to that of the com-

mercially available weakly acidic cation exchanger. This resin removes ammonia from the water efficiently and the uptake is reversible. Ammonia is recovered in the form of ammonium sulphate the concentration of which could be built up to 16 per cent by recirculating the used regenerant. The ammonium sulphate solution can be used in the process of the manufacture of fertilizer and the problem of the disposal of the waste regenerant does not arise. The operating cost, considering the consumption of chemicals only and taking into account the value of recovered ammonium sulphate, works out on a laboratory scale experiment to Re. 1.00-Rs. 1.50 per 1000 litres. The process developed has good application potential, not only for the pollution abatement, but also for the recovery of the pollutant in the form of a useful salt (Table 1).

(ii) Mercury removal from the waste water of chlor-alkali industry

The installed capacity of the chlor-alkali industry in our country for the manufacture of sodium hydroxide is 7.8 lakhs tonnes per year. There are 35 chlor-alkali plants in the country of which 24 plants use the mercury cell process. In the properly supervised and controlled plants mercury loss of 70-80 g per tonne of caustic soda has been reported. While in the old and poorly managed plants this figure reach as high as 250-300 g of mercury per tonne of caustic soda. On this basis the total mercury thrown out by the chlor-alkali industry is mind-boggling. The main points where mercury is found, in one form or the other, in chlor-alkali industries are (i) in the hydrogen gas which comes out of the cell, (ii) in caustic soda, (iii) in the chlorine gas, (iv) in the brine, (v) in the sludge from brine purification and (vi) in the effluent waste water. The amount of mercury present at each of these cases depends on the precaution being exercised in the industry. Mercury poisoning causes a serious physical impairment of human bodies as a result of the paralysis of the central nervous system. Various agencies have specified the maximum permissible limits of mercury in the effluents. In India, the Central Board for Prevention & Control of Water Pollution, New Delhi, stipulated a concentration of 0.01 mg/litre in the treated effluent.

A mercury selective ion-exchange resin is developed in the Institute which shows higher exchange capacity, porosity, surface area and greater mercury uptake. It has better dimensional stability and non-fouling type of polymer matrix and is thus ideally suited for the removal of mercury from the waste water. The uptake of mercury depends on the concentration of mercury in the water. In one particular case the resin could remove mercury from 1300 bed volumes of wa-

Table 1—Removal of ammonia from the fertilizer industry effluent

Resin exchanger	<i>Methacrylic acid</i> based cationic
Chemical cost	1.0 to 1.5 Rs/1000 lits
Pollutant NH ₃ is recovered as	(NH ₄) ₂ SO ₄
Life of the resin	20 years (5% replenishment)
NH ₃ in the effluent	Any quantity
NH ₃ in the treated stream	5 ppm

Table 2—Chlor-alkali industry: Removal of mercury from waste water

Limit for pollution control	0.01 ppm
Resin	Styrene based macroporous polymer; styrene disulphide
Chemical cost of treatment	Rs 3 to Rs 4/1000 litres
Hg in the effluent	Any conc.
Hg in the treated stream	0.01 ppm
Life of the resin	20 years (5% replenishment)

ter containing 8 mg of mercury per litre and the entire loaded mercury could be removed in 3.5 bed volumes of the regenerant. The resin shows reversible uptake of mercury. The operating cost of the treatment considering the chemicals consumption only works out to be Rs. 3 to Rs. 4 per 1000 litres on a laboratory scale experiment. The operating cost can still be brought down if the cost of the recovered mercury is taken into consideration (Table 2).

(iii) Phenolics from the waste waters of refineries/ carbonization plants/resin manufacturing units

Phenolics in waste water are harmful pollutants which originate as byproduct from several major industries like pulp and paper mills, carbonization plants, petroleum refineries, tanning industries, resin manufacturing units etc. Phenol concentration of more than 0.005 mg/litre imparts colour and odour to water and at a level of 2 mg/litre, it is toxic. The quantity of the waste water and its phenolic content varies from industry to industry. For instance, in a plant of low temperature carbonization under normal operating conditions, the waste waters generation is of the order of 0.13 to 0.15 m³/tonne of coal carbonized. This waste has a very high pollution potential as it contains phenolics, free and fixed ammonia, thiocyanates, thiosulphates, cyanides and sulphides. Phenolics constitute mono, di and trihydric phenols, cresols and xylenols. The waste water of Gujarat Aromatics Project at Ankaleshwar contains toxic constituents like phenols and other

organic matter. Effluents from synthetic resin manufacturing plants contain phenolics, chlorides and sulphates in dissolved state and sometimes petrochemical solvents. There is a wide variation in the pH of the effluent ranging from 2-3 (low) to 11-12 (high).

Among the various methods adopted for the removal of phenol, polymeric adsorbents are very promising. Their efficiency for the removal of phenolics and their subsequent recovery is exceptionally good. The concentration ratio that can be achieved is very high. The required equipment is simple to design and the operation is usually trouble free. The sorption can be carried out at ambient temperature and the space requirements are small. Very stringent specifications for pollution control regarding the quality of the effluent can be attained by the use of porous polymeric adsorbent. One such porous polymeric adsorbent developed from acrylonitrile matrix removes phenol from 145 bed volumes of the water containing phenol and all the loaded phenol is recovered in 3 bed volumes of methanol. Phenol as well as methanol is recovered by distillation. The loading of phenol depends on its concentration and the uptake is reversible (Table 3).

(iv) Dyes from the waste waters of textile industry

Textile dyeing and printing industries have rapidly developed in and around Jetpur town in Gujarat State. The disposal of the waste water of saree printing industries is posing serious problem as the receiving river stream has become coloured over a stretch of several kilometers and the well waters in the vicinity of the town are coloured due to the presence of reactive dyes discharged by these industries. An electrolytic decomposition technique has been developed in the Institute and the waste water could be decolourised in a continuous manner using an electrolytic cell designed and fabricated in the Institute. The electrical energy consumption is 3-4 kwh per kg of the dye removed when the electrolytic content of the printing bath solution is 10 per cent. The decolourised bath solution can be reused for the printing purpose (Table 4).

(v) Processing of the pulp and paper mill waste water by reverse osmosis for the pollution control

The pulp and paper mills consume large amount of water. A mill processing 150-500 tonnes of cellulose pulp normally uses 5 to 50 million gallons of water daily. This waste water can be processed by reverse osmosis technique after suitable pretreatment like sedimentation, filtration and pH adjustment to recover water for reuse and the concentrate portion resulting

Table 3—Phenolics from refineries/carbonization plants/resin manufacturing units

Phenol conc. of more than 0.005 ppm imparts colour and odour to water and at 2.0 ppm level it is toxic.

Resin	Porous polymeric adsorbent based on acrylonitrile matrix
Phenol recovery	By methanol
Life of the resin	20 years (5% replenishment)
Final phenol level in the treated effluent	< 0.005 ppm

Table 4—Dyes from the waste waters of textile printing industry

Polymeric adsorbent	Acrylonitrile for rhodamine-B nylon saree printing
Regeneration	Acetone, MeOH or EtOH
Life of the resin	
Specific ion-exchange resins developed for	
(1) Chromium	
(2) Arsenic	
(3) Lead	

in this treatment may be used for the recovery of chemicals like caustic soda or sodium sulphate.

A waste water sample procured from M/s Central Pulp Mills Ltd, Songad, Surat could be treated by reverse osmosis using standardised cellulose acetate membranes at an operating pressure of 600 psi for 50 per cent recovery. It is observed that B.O.D. and C.O.D. from the waste water could be effectively removed and the waste water is suitable for discharge into inland waters or for reuse in industry¹.

(vi) Processing of cheese whey by ultrafiltration/ reverse osmosis for the pollution control

Cheese whey is the fluid portion of the milk obtained after coagulation of casein during the manufacture of cheese. It contains half of the milk solids—most of the lactose, 20 per cent of the protein and most of the vitamins and minerals. Even though 70 per cent of the nutritive value of the milk lies in the whey, it is often disposed off as a waste and poses a serious pollution problem. At present whey is processed by evaporation and spray or drum drying. These techniques are expensive owing to the low initial concentration of solids. Besides, the high salt and lactic acid content of dried whey prevents the product being marketed for human consumption. Ultrafiltration technique appears to be attractive since it has the capability of fractionating the proteins from the unwanted salts, lactic acid and lactose. Lactose which contributed to the high C.O.D. level of protein-free filtrate, can be concentrated and removed by reverse osmosis process. A plain defatted cheese whey procured from M/s

Amul Dairy, Anand could be treated by the twin techniques mentioned above and the results illustrate that about 70 per cent of the protein and 80 per cent of the lactose originally present in the cheese whey could be recovered and the permeate from the reverse osmosis process can be reused within the dairy as fresh water. Thus, not only the pollution problem in the dairy industry is solved but valuable proteins, lactose and water are recovered².

(vii) Processing of the rayon mill effluent by reverse osmosis for pollution control/recovery of sodium sulphate

Rayon mill effluent mainly contains sodium sulphate with considerably less amounts of zinc sulphate and sulphuric acid and thus poses a serious disposal problem. Such waste waters procured from M/s Century Rayons and M/s Gwalior Rayons could be treated by the reverse osmosis process. The pretreatment involves neutralisation of the acid with sodium carbonate and filtration through sand filters. The results obtained denote the efficiency of the technique to treat such effluent and the recovery of sodium sulphate. The cost analysis shows the energy consumption is to the extent of 6-8 kwh per 1000 litres of the waste

water for the concentration of sodium sulphate as against 1.25 tonnes of steam required in the evaporation method. Sodium sulphate is recovered from the concentrate by chilling at 0°C and drying the Glauber salt thus obtained at 110°C³.

A tentative cost estimate indicates that the membrane processes are more favourable compared to and competitive with the conventional methods of water treatment and water pollution control as practised today. There is a growing awareness in the chemical industry to adopt membrane technology in many of their separation processes involving separation, concentration or purification of chemicals, recovery of chemicals and/or reuse of water and pollution control. It is thus envisaged that in the near future membrane will find its legitimate place not only in the chemical industry but in other spheres like bio-technology and food processing.

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A high capacity steel shell lime shaft kiln for building industry

C L Verma, S K Jain & R K Yadav

Central Building Research Institute, Roorkee 247 667

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The Indian building lime industry falls under the category of small and medium scale sector employing kilns of capacities generally upto 10 tpd. On account of the requirements of changed environment and some inherent drawbacks of the existing masonry kilns, a steel shell lime shaft kiln of 20 tpd capacity has been designed. The process engineering aspects and mechanical design features of the same have been detailed with due cognizance to pollution control measures. It is proposed that the existing low capacity country kilns may be replaced with this moderately high capacity kiln in congested and highly air polluting lime manufacturing centres in the country.

Lime is an industrial chemical of significant importance which finds extensive applications in a multitude of Building, Chemical Metallurgical and Allied process industries. It is produced by the endothermic process of calcination of lime stone, the heat being supplied by the combination of fuel, at elevated temperatures usually exceeding 900°C under atmospheric pressure conditions. The process is effected in a lime kiln. The various interphase and mass exchange phenomena vis-a-vis chemical reactions occurring inside a kiln are quite complex in nature and have to be understood properly for incorporating some controls on the kiln with a view to achieving fuel economy and uniform quality of product¹.

The Indian building lime industry, by and large, works in the small scale and cottage sectors. About 5 million tonnes of lime is being produced in India per annum out of which about 2 million tonnes are produced in the building industry. The units in the small and cottage sectors are distributed all over the country and the same can be seen outside the municipal, town, village limits in the proximity of habitation. Most of the units in the small-scale sector produce about 5-10 tonnes of lime per day.

Characteristics of Small Scale Lime Kilns

The low capacity kilns require less capital investment and working expenses. These kilns do not require sophisticated instruments and in most of the cases, even power is not needed. However, these kilns suffer from the following inherent drawbacks² :

- (i) Low productivities
- (ii) Low thermal efficiencies
- (iii) No proper controls on the process
- (iv) Poor quality of the end product

- (v) Environmental pollution hazards
- (vi) Reduced life span involving high maintenance costs

National Status

The improved vertical lime shaft kiln constructed in masonry and based on intermediate technology is rather a recent development in India and its use was earlier advocated by the Central Building Research Institute, Roorkee and Khadi and Village Industries Commission, Bombay for the manufacture of building lime for smaller capacities of production. Charging and discharging mechanisms are manual in the conventional lime shaft kilns³.

Based on field surveys and detailed investigations on typical lime kilns at several important lime manufacturing centres, the lime kilns for capacities of 5, 10 and 15 tonnes per day were designed at the Central Building Research Institute, Roorkee. Kilns of improved designs have been successfully installed and commissioned in different parts of the country. The salient features of the improved designs are as follows^{4,5}.

- (i) Mixed-feed vertical masonry shaft (steam coal fired)
- (ii) Cylindro-conical structure with uni-inner lining of fire bricks
- (iii) Continuous operation – 2 to 3 shifts per day
- (iv) Uniform natural draft
- (v) Manual as well as mechanized charging
- (vi) Fuel economy upto 15 per cent over conventional kilns
- (vii) Suitable for dolomitic and calcitic limestones
- (viii) Better quality of end product

- (ix) Mild steel rings and angle iron outer facing for 5 tpd capacity kilns
- (x) RCC ring beams and columns on the outer periphery of the 10 and 15 tpd capacity kilns

A low cost mechanical charging device to handle about 20 tonnes of material per day has been designed for feeding the mix of limestone and coal into the kiln. The labour requirement is reduced by 50 per cent while the total charging time is reduced by about 40 per cent³.

Requirement of Steel Shell Kiln

There is a huge gap between the present production of lime and its likely demand. Although no reliable statistics are available, an annual short fall of as much as 7 to 8 million tonnes was envisaged during the eighth five year plan. The lime industry has felt the necessity of upgrading the kilns in order to increase production and bring them on more scientific footing. Thus the work on design and development of 20 tpd capacity steel shell lime shaft kiln was taken up at the Central Building Research Institute, Roorkee. The anticipated advantages of the steel shell structure over that of the masonry are as follows :

- (i) Prolonged life and durability
- (ii) Crack-free structure
- (iii) Higher production capacities
- (iv) Lower cost of production
- (v) Thermally efficient
- (vi) Amenable to mechanisation and instrumentation
- (vii) Better provision for adoption of pollution abatement measures

Although the steel shell lime kiln technology has been developed at the Federal Republic of Germany, Switzerland, Japan, Italy, etc. yet the designs are either patented or proprietary in nature. Hence, the work was taken up to bridge the prevalent gaps in the field.

Process Engineering Design

Field studies on some of the existing high capacity lime kilns in sugar and steel industries were carried out for the collection of relevant design and performance data. Systematic studies on the effect of various process parameters on the design and performance of the lime kiln were carried out and results were utilized in fixing up the process engineering design features such as heights of the various zones and diameter of the lime kiln¹. The thickness of the steel shell is calculated on the basis of the various types of loads and thermal stresses to be exerted on the kiln, keeping in view the permissible strength for mild steel shell.

Table 1—Specifications of the lime kiln

No.	Item	Specification
1	Shape	Double conical
2	Height	16.0 m
3	Average inner diameter	3.5 m
4	Construction material	M.S. sheet
5	Thickness of steel shell	10 mm
6	Thickness of fire bricks lining	23 cm
7	Thickness of insulating bricks	11.5 cm
8	Limestone coal ratio by weight	5-6

Poke and observation holes are provided throughout the height of the kiln arranged at suitable intervals for effective operational control of the kiln. Brief technical specifications of the 20 tpd lime kiln are given in Table 1.

Mechanisation Aspects

Mechanical charging devices are used for hoisting the mixed-feed of limestone and coal to the top of the kiln. These devices may be continuous type of belt conveyor, bucket elevator, skip hoist, etc. as per site layout³. However, skip hoist has been considered to be the most appropriate system for the charging operation. The hoisting unit consists of a head assembly, made up of motorised reducer coupled to the winding drum through an electromagnetic brake. The raw materials are to be fed to the kiln top into a receiving hopper. For high lift and larger lumps of limestone, a skip hoist is considered more suitable. Bell and cone arrangement is proposed for feeding the raw material into the kiln. The bell can be lifted either manually or by a small motor. A central discharge arrangement is being envisaged for the withdrawal of lime. Figure 1 depicts the details of the steel shell lime shaft kiln. The bell and cone arrangement for feeding of the raw materials into the kiln is shown in Figure 2. The kiln is supported on four fabricated steel stands arranged to be placed on concrete foundation blocks. Five supporting rings are provided within the shell plate for sustaining the refractory lining (fire and insulation bricks) of different heat zones to enable renewal of the refractory lining of any zone without disturbing the others.

Provision for Pollution Control

Reduction in pollution of the environment is the crying need of the present times. Several governmental bodies, pollution control boards along with international environmental agencies have been advocating the employment of pollution control measures in various industries. Even though lime is a

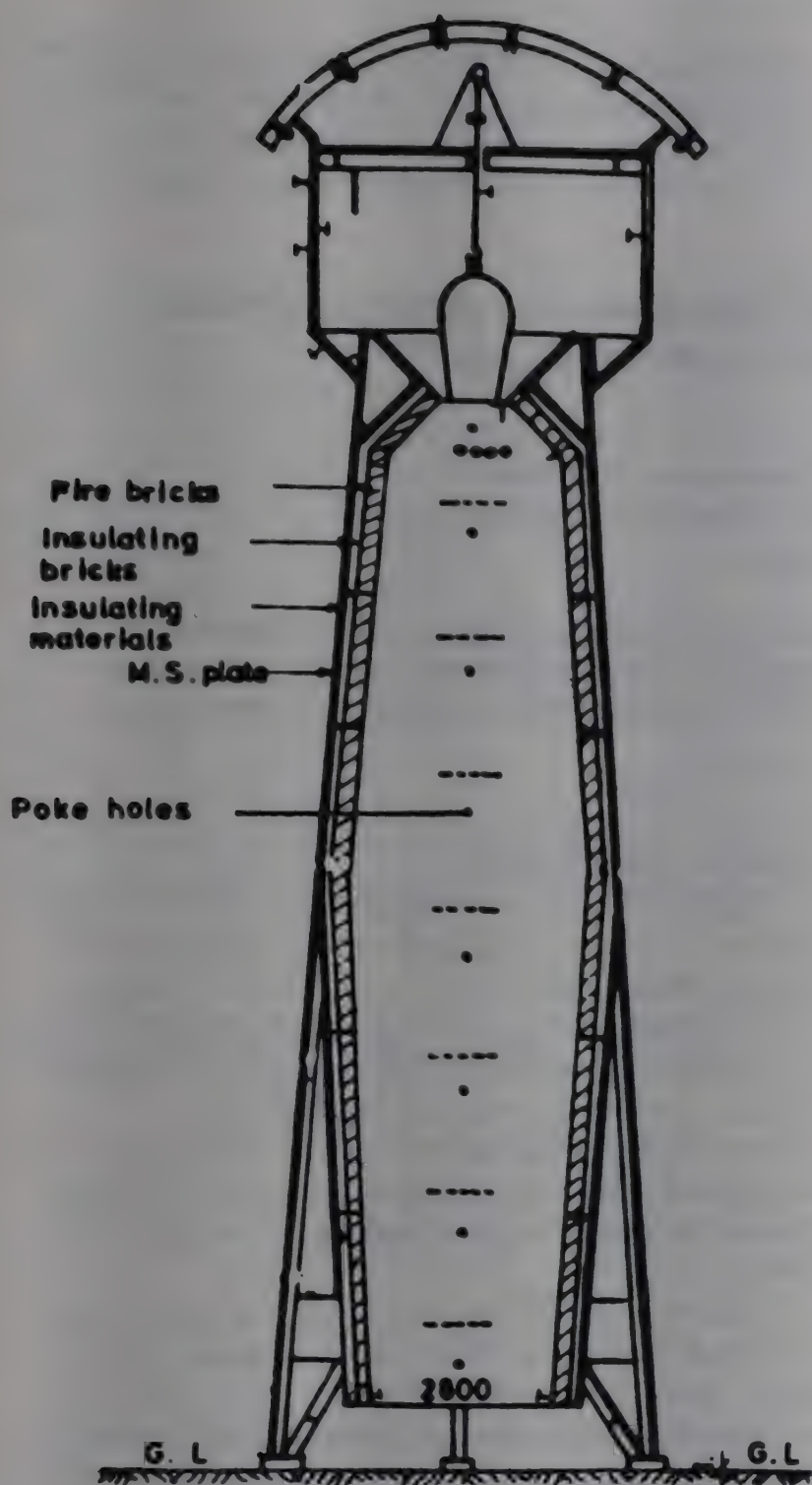


Fig. 1—Design of 20 tpd capacity steel shell lime kiln

low polluting industry yet suspended particulate matter (comprising kiln dust and hydrocarbon volatiles) has been identified to be the major pollutant being emitted from the coal fired lime kilns⁶. Out of the various pollution abatement devices, viz inertial separators, dry and wet scrubbing systems, fabric filters, electrostatic precipitators, etc. a water scrubbing system, chimney with hood along with an I.D. fan and a net work of piping, ducting, fittings, etc. has been designed and developed for the control of pollution from the lime shaft kiln. The control unit can be fixed at the top portion of the kiln and flue gases after purification can be discharged to the atmosphere through the chimney of the system.

Concluding Remarks

A coal fired steel shell lime shaft kiln of high capacity has been designed for prospective users of

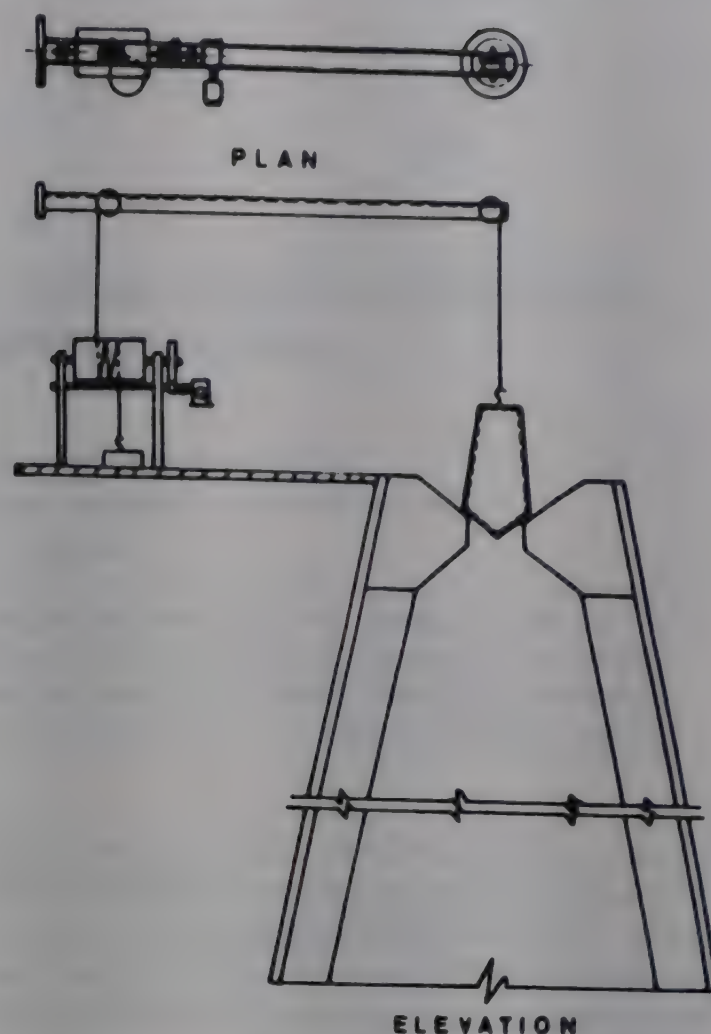


Fig. 2—Feeding device for shell lime kiln

the Indian building lime industry. The kiln is well equipped with semi-mechanization features and the same is also amenable to a fair degree of instrumentation, process vis-a-vis pollution control measures. The kiln is thermally efficient with low maintenance and operational costs. The installed cost of the kiln with all accessories is projected as Rs.15.00 lakh. It is envisaged to fulfil the requirements for calcination of high calcium as well as dolomitic limestones.

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Tetrabromobisphenol-A as fire retarding agent for epoxy polymers, optimum parameters for its synthesis

M Q Parwez, R K Raina, G N Rastogi and D A Dabholkar
Shriram Institute for Industrial Research, 19, University Road, Delhi 110 007

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Tetrabromobisphenol-A, an important fire retarding agent in epoxy polymers was prepared by the bromination of bisphenol-A in various solvent media. Reaction parameters affecting the yield and the purity of tetrabromobisphenol-A were studied and optimised. Product obtained was characterised for its bromine content and melting point.

Application of polymers in the field of electronics and other critical sectors demands the material to be fire-retardant. Epoxy resins an important class of thermosetting polymers suffer from the draw back that these cannot be used in many applications which require fire retarding property. For improving upon this property a considerable work has been done by using HET anhydride as the curing agent, or by incorporating quantities of antimony trioxide or to use a non-reactive phosphorous containing diluent. It has been seen that all these methods lead to deterioration in the physical properties of the system or limit the choice of curing agent and fillers normally available. To improve upon such properties and add further thermal stability without sacrificing the well balanced properties of epoxy polymers an introduction of rigid chains by way of copolymerisation seems necessary.

Tetrabromobisphenol-A (TBBA) appears to serve the purpose best in light of its bromine liberation only at decomposition temperature. Though a considerable literature is available on its preparation but those are mostly in patented form¹⁻⁴. Asadorian and Tigner⁵ have done a considerable work in the synthesis of TBBA in halocarbon and water as solvent medium. Critical parameters, reported in the literature and affecting the reaction to make the process commercially viable, lie in broad ranges and are thus difficult to practice commercially. Knowing the potential use of this versatile brominated bisphenol-A in other polymers such as polycarbonate resins, unsaturated polyester resins and polyurethanes as fire retarding agent, it has been found appropriate to study the effect of various reaction parameters on the yield and product characteristics in synthesis process.

Materials and Method

Bisphenol-A (commercial) supplied by M/s Shah Research Laboratory, Bombay was washed twice to remove the colour and give a product of melting point 156°C. Washing was done in warm 28 per cent aqueous solution of acetic acid followed by filtration and couple of washings with distilled water.

Bromine from Qualigens Fine Chemicals was used as received. Methanol, acetic acid and carbon tetrachloride laboratory reagent grade were distilled before use.

Bisphenol-A (BA) was dissolved in a solvent in a four neck flask equipped with a condenser, a dropping funnel, a thermometer and a stirrer. Bromine was added under constant stirring while the temperature of the mixture was maintained between 5-15°C with the help of ice bath and rate of bromine addition. After complete bromine addition ice bath was replaced by a water bath and the reaction mixture was refluxed for 90 min. When methanol was used as a solvent, CH₃Br formed during the reaction was passed through a series of scrubbers and collected in ether solvent as a by-product. The reaction mixture was then cooled to room temperature and filtered. The solid cake was washed with water until free of hydrogen bromide and then dried in a vacuum even at 40 to 45°C.

The product was purified by recrystallisation from isopropanol and analysed for melting point, IR spectrum and bromine content. Bromine content was determined by ASTM by E-442 Oxygen flask method.

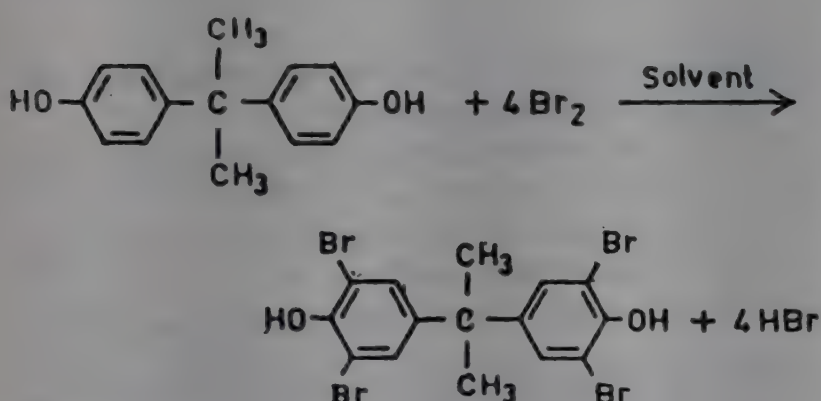
Results and Discussion

The dynamic modulation of the process parameters was studied by varying various input parameters in order to determine the economic feasibility of the

process for the preparation of TBBA. For this, a series of experiments were conducted to evaluate the effect of a particular parameter on the quality and quantity of the product while keeping all other conditions constant.

Effect of molar ratio of bromine to bisphenol-A

Molar ratio of bromine to BA was varied from 2:1 to 6:1 keeping the other reaction parameters like reaction temperature (65°C) and time (90 min) as constant. In all these experiments methanol was taken as solvent medium. From Fig. 1 it can be seen that with the increase in ratio of bromine to BA, upto 4:1 the yield increases substantially, reaches an optimum at 4.04:1 and comes down afterwards. At the ratio of 4.04:1 the product is having the desired bromine content and melting point (Table 1). Theretically also it is expected that for the conversion of BA to TBBA four bromine electrophiles should substitute four hydrogen atoms of BA as shown in the following reaction.



The low yield, low melting point and low bromine content of the products of reactions having bromine to bisphenol ratio less than 4:1 suggests that some BA remained unconverted to TBBA. Slight increase in ratio of bromine to BA from 4:1 to 4.04:1 further increases the yield by 1 per cent and brings the bromine content nearer to theoretical value of 58.8 per cent. Further increase in the ratio results in decrease in the yield but gives the product with no significant change in its melting point. This indicates that at the ratio of bromine to BA higher than 4.04:1 acid decomposition of BA and TBBA takes place producing smaller soluble fragments which remain in the filtrate.

Effect of reaction time

To study the effect of reaction time on the yield and other properties of TBBA experiments were carried out in which the reaction time was varied from 30 to 120 min. In all these experiments methanol was taken as solvent medium and other parameters such as mole ratio of bromine to BA (4.04:1) and reaction

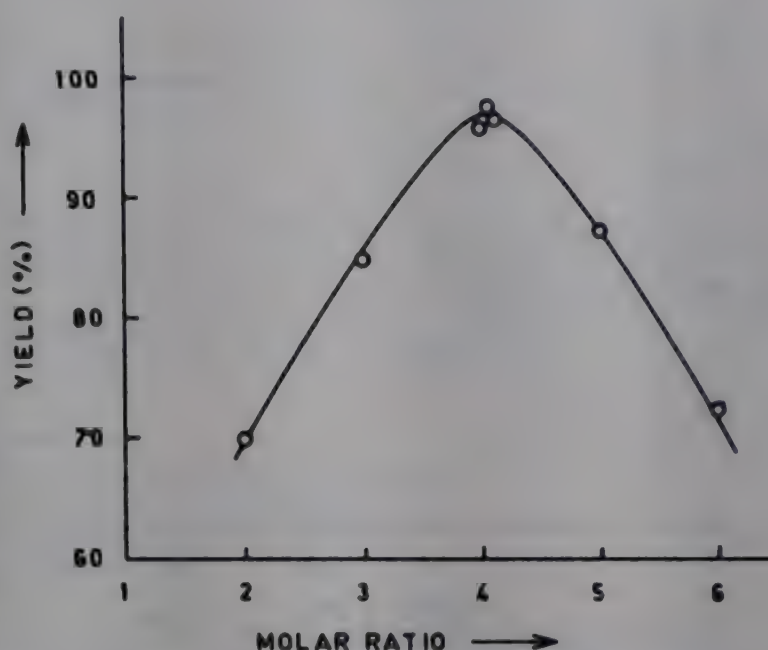


Fig. 1—Effect of molar ratio of bromine to BA on yield of TBBA

Table 1—Effect of molar ratio of BA to bromine on yield and purity of TBBA

Molar ratio of BA to bromine	Yield (per cent)	M. Pt. (°C)	Bromine content (per cent)
1:2.00	70	174	89.6
1:3.00	85	175	44.0
1:4.00	96	181	58.0
1:4.04	98	182	58.7
1:4.08	97	182	58.8
1:5.00	88	181	58.9
1:6.00	73	181	59.3

temperature (65°C) were kept constant. Here, the reaction time means the time of refluxing the reaction mixture after complete addition of bromine. From Fig. 2 it is clear that as the reaction time increases from 30 to 120 min, yield of product goes up. However, beyond 120 min the yield tends to decrease. The purity of the product was also found to be high upto the reaction time of 120 min. Beyond this period the quality becomes poorer (Table 2). This might be due to the debromination of TBBA on refluxing the mixture for longer period.

Effect of solvent medium

To establish the effect of solvent medium on the synthesis of TBBA, the reactions were carried out in different solvent media keeping the molar ratio of bromine to BA as 4.04:1.

In the first experiment, 60 per cent acetic acid in the molar ratio of BA to acetic acid as 1:10 was taken as

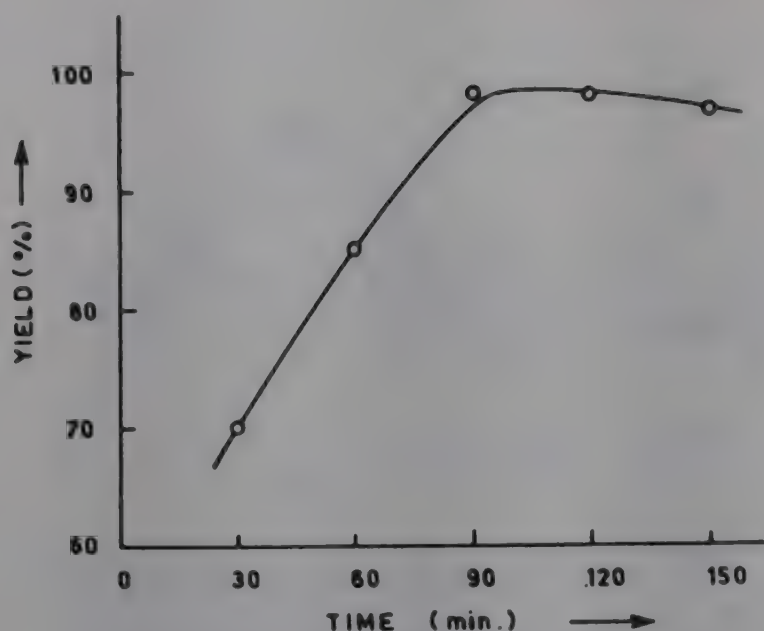


Fig. 2—Effect of reaction time on yield of TBBA

solvent medium. The reaction mixture was refluxed for 90 min after completion of bromine addition. The product of this reaction was found to be white in colour having bromine content slightly higher than the theoretical value. The higher bromine method indicates that some free bromine remained entrapped during the process.

In 2nd experiment, carbontetrachloride in the molar ratio of BA to CCl_4 as 1:6 was taken as solvent medium. Water about 50 per cent of the volume of CCl_4 was used as a suspending agent for BA. The reaction mixture was refluxed for 90 min. The product of this reaction was found to be slightly off white having the melting point within the range but substantially low bromine content.

Finally, in the 3rd experiment methanol in the molar ratio of BA to CH_3OH as 1:20 was taken as solvent medium. The yield of methyl bromide an important by product collected in ether was found to be about 60 per cent of the theoretical value. TBBA obtained by this process was found to be slightly off white having melting point and bromine content within the expected limits.

Comparing the results of these three experiments it is clear that methanol is the most suitable solvent medium to get TBBA of high purity and yield (Table 3). Economically CH_3OH is also the preferred solvent because it gives a valuable by product i.e. CH_3Br , which can be used for extermination of insects, fumigation of food commodities, fire extinguisher for aeroplane engines and in methylation reactions.

Conclusions

From the studies carried out on effect of various reaction parameters on purity and yield of the pro-

Table 2—Effect of reaction time on the yield and purity of TBBA

Reaction time (min)	Yield (per cent)	M. Pt. ($^{\circ}\text{C}$)	Bromine content (per cent)
30	70	172.0	36.0
60	85	176.0	45.0
90	98	182.0	58.7
120	98	182.5	58.8
150	97	180.0	56.2

Table 3—Effect of solvent on yield and purity of TBBA

Solvent used	Yield (per cent)	M. Pt. ($^{\circ}\text{C}$)	Bromine content (per cent)
Acetic acid	87	180	59.1
Carbontetrachloride + water	77	179	52.2
Methyl alcohol	96	179	58.4

duct in the synthesis of tetrabromobisphenol-A, the following observations were made.

- Use of methanol as a solvent results in high purity and yield of the end product (TBBA).
- The optimum ratio between bisphenol-A to bromine was found to be 1:4.04.
- Bromination of low temperature gives better

quality product and also high yield. Preferably the temperature of the reaction mixture should be maintained below 15°C during bromine addition.

- It was observed that refluxing reaction mixture for about $1\frac{1}{2}$ hr seems to be the optimum time required for completion of the bromination.

Acknowledgement

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A new process for production of super-clean coal for industrial boilers by organosolvo-refining technique — A case for clean coal technology transfer to industries for setting up coal refineries

D K Sharma

Fuels and Biofuels Engineering Laboratory, Centre for Energy Studies,
Indian Institute of Technology, Delhi, New Delhi 110 016

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Indian coals contain 5-55 per cent mineral matter content which leads to several engineering problems during combustion of coal besides causing environmental pollution. Physical beneficiation techniques result in only partial cleaning of coals as mineral matter is finely disseminated in Indian coals. An advanced process for the chemical cleaning of coal by the convenient organosolvo-refining technique has been developed. The use of hydrogen and high pressure has been avoided. Also, coal derived solvents have been used. A semi-continuous trickle bed flow-through extractor has been designed and fabricated to process up to 1/2 kg of coal feed. Extraction times have been reduced by stepwise successive extraction techniques. The residual coals obtained were found to retain appreciable amount of volatile matter and were found to be friable and free flowing and fit and reactive enough for pulverized fuel and fluidized bed combustion, steam gasification and carbonization. The residual coals may be gasified to generate power by integrated coal gasification combined cycle power generation. Several options for the use of super-clean coal (an environmentally clean and high heating value fuel) obtained, have been suggested. This advanced technology of coal cleaning has been recommended for further development and transfer to industries for commercialisation by setting up coal refineries there.

Oil reserves of the world are limited and these are expected to last for another 60 years or so at the present rate of consumption. However, with increase in world population, and with increase in the industrialisation of developing nations and with a consequent increase in the standard of living of masses, the rate of consumption of oil is on the increase. Energy conservation measures can delay but these can not stop ultimate total depletion of oil and natural gas reserves sooner than thought. The situation is more grim as far as India is concerned. The oil and natural gas reserves of India are expected to last for 20 years. Therefore, the day is not far when India may have to depend exclusively on import of oil in spite of meagre foreign exchange reserves. Fortunately, India has large reserves of coal which are expected to last for more than 350 years. The only problem with the use of these coals is their high mineral matter content which vary from 5 per cent to as high as 55 per cent. The major users of coal in India are thermal power stations. Most of these plants have pulverized fuel firing systems. The pulverized fuel burners of these plants were designed to handle mostly the coal having at the most 25 per cent mineral matter (MM) contents. These thermal power stations are mostly firing E, F and G grades coals with average

MM contents of 25 to 45 per cent. This is leading to several major problems.

Major Engineering Problems in Coal Combustion due to High Mineral Matter Contents in Coal

The major problem is the generation and disposal of fly ash. On average around 50 million tons of fly ash is being generated in thermal power stations in India by burning roughly 150 million tonnes of coals annually. Disposal of this ash is currently a major problem threatening the generation of power by burning low grade Indian coals. This is expected to increase to 85 million tons by the turn of the century. There are following other major engineering problems caused by burning high ash low grade coals in thermal power stations.

- (i) Bigger size boilers are required with a consequent reduction of boiler efficiency.
- (ii) Bigger and larger number of plant auxiliaries are required.
- (iii) Increased auxiliary oil consumption.
- (iv) Increased auxiliary power consumption.
- (v) Increased size and capacity of coal handling plant and increased coal and ash handling costs.
- (vi) Reduced plant load factor.
- (vii) Increased transportation cost.

(viii) Increased size and cost of electrostatic precipitators.

(ix) Reduced reliability and availability of plant.

(x) Corrosion and erosion of boiler tubes, superheaters, economisers, induced draught fans and plugging of air preheaters.

(xi) Slagging and fouling due to ash.

(xii) Problems due to Na, K, in fly ash in reducing heat transfer rates.

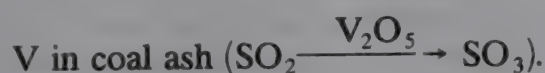
(xiii) Release of toxic and hazardous elements in fly ash to increase environmental pollution and other health and ecological problems.

(xiv) Increased outages and downtime.

(xv) Loss of heat in melting and fusing of coal ash and clinker formation, requiring more coal to be fired per unit power generation, thus raising CO₂ level in the environment to increase green house effect.

(xvi) Uneven burning of coal particles.

(xvii) Corrosion due to acid formation by the presence of



(xviii) Less combustion efficiency of coal.

(xix) Increased maintenance costs.

(xx) Increased operational cost.

There can be several other problems in the combustion of low grade coals, caused by the high MM contents of coals as ash handling is an expensive, dirty and dusty operation. In fact, environmental impact assessment studies have shown the rise of environmental pollution level in the areas surrounding the thermal power stations¹⁻³. A recent study has reported the rise of toxic minerals such as copper, lead, zinc, cobalt, cadmium and manganese in the milk of cattle in the areas around thermal power stations¹. The hazards of pollution caused by the combustion of coals, especially by the microconstituents of coals such as As, Pb, Hg, Zn, Cu, Co, Ni, Mn, Se, Cd, V, Na, K, etc. have been realised lately in USA⁴⁻⁶. Several studies have been initiated for the precombustion control of hazardous air pollutants in USA, even though US coals are low ash (MM) containing coals⁴⁻⁶. The situation is more alarming in India.

The higher MM contents of low grade Indian coals cause problems not only in direct combustion but also in other coal conversions such as, gasification, liquefaction, carbonization and in every method of utilization of coals. Therefore, there is only one option and that is if Indian coals are to be utilized these should be refined and cleaned before use^{7,8}.

Beneficiation of Coals

The most established coal washing techniques such

as Baum jigs, Dense media (Chance Cone and Cyclone), Tabling and Froth Flotation are being practised for cleaning coking coals for steel plants. However, steel plants use premium (A, B and C) grade of coals with ash content less than 20 per cent. In fact, classical clean coal preparation techniques depend upon exploitation of specific gravity differences in some form or other to obtain a trade-off between partially clean coal, middlings and rejects, the reduction in MM contents of the clean coals being only limited, and that too at the cost of disposal of middlings and rejects.

In fact, the mineral matter in Indian coals is finely disseminated and firmly bound in the organic coal matrix. It is difficult to remove this by conventional coal washing techniques even after finely pulverising the coals. The emerging coal washing techniques such as spiral separators, column flotation, oil agglomeration, oleoflotation and reverse froth flotation, etc. also result in only partially cleaning the low grade Indian coals with mineral matter dispersed finely within the organic coal matrix and there is a strong chemical affinity of MM with organic matrix. Physical beneficiation is only partially successful also because of the presence of near gravity material in Indian coals mostly. This shows that only cleaning techniques where solvent can penetrate the solid coal to leach the mineral matter held in the organic coal matrix, may be successful in cleaning low grade Indian coals.

Chemical Cleaning of Coals

Several advanced chemical cleaning techniques for demineralising the coals are emerging⁹⁻¹¹. Most of these techniques employ inorganic reagents, mostly alkalis and acids to leach the MM contents from coals¹². The major problem with these techniques is the material of construction of reactors as alkalis and acids are highly corrosive. Moreover, these are also costly and their recovery, regeneration and recycle is questionable. The higher MM contents of coals react with these. In some cases, the use of high pressure and elevated temperatures is also a problem^{11,12}. Some times the Na and K, etc. salts get contaminated with coal and these unfavourably increase the rate of combustion of coals.

Since most of the American, European, and Australian coals are low MM containing coals, therefore, not much research on demineralisation of coal has been carried out by researchers there. Lot of work on desulphurisation of coals has been conducted there. This shows that Indian scientists, technologists and engineers may have to take a lead in this direction as demineralisation of coals is a compelling need of Indian industry alone.

Organosolvo-Refining of Coals

A parallel approach towards the demineralisation of low grade Indian coals could be to recover the premium organic matter from coals by solvent refining, i.e. extraction techniques. The conventional techniques of solvent refining employ the use of high hydrogen pressure at elevated temperatures by using preferably hydrogen donor solvents^{13,14}. This process produces a clean coal, however, the use of hydrogen makes the process costlier. Moreover, the use of high pressures renders the process inconvenient for normal industrial processing.

Research work on the development of a convenient, efficient and cost-effective process for organosolvo-refining of low grade Indian coals was undertaken by the author 16 years back¹⁴⁻⁴⁰. The driving aim was to avoid the use of high pressure and elevated temperatures above 350°C.

In order to keep the costs low, the use of hydrogen gas was not included. Extraction studies of several Indian coals such as Assam, Samla, Talcher, Godavari, Chinakuri coals and of some coals from local Thermal Power Stations along with those of Neyveli and Kutch lignites were undertaken¹⁴⁻⁴⁰. Several organic solvents such as hexane, toluene, phenol, tetrahydrofuran, pyridine, dimethyl formamide, dioxane, tetralin, decalin, dodecane, acetone, methanol, ethanol, butanol, glycerol, benzene/methanol, chloroform, ethyl acetate, ethylenediamine, monoethanolamine, triethylamine, quinoline, creosote oil, cetene, cetanol, phenol and dodecanol, etc.^{14,16} were used for these extractions^{14,16}. Extractions of Indian coals in most of these solvents were found to be less than 20 per cent. It was decided to degrade, derivatise and depolymerize the coal to enhance the extractability of Indian coals^{14,21-35,39}. Most of these techniques resulted in increasing the extractability of coals up to 90 per cent, but these also increased the cost of the process^{14,21-35,39}. The details of these studies would be published separately.

It was decided to chemically disintegrate and disaggregate the coal by using moderately (high) boiling solvents such as quinoline, anthracene oil, creosote oil, kerosene and liquid paraffin, etc. The aim was to exclude the use of costly chemicals and in order to economise the process, the use of only the coal derived chemicals under ambient pressure conditions was made. The use of solvents such as anthracene oil (AO), quinoine (Qn) and liquid paraffin (LP) was found to be encouraging and interesting. About 38 per cent Assam coal was found to have been extracted in AO after 24th of extraction. The use of Qn resulted in the extraction of 20 per cent

Assam coal after 2 h and the yields remained constant after 2 h. About 20 per cent Assam coal was rendered extractable in LP after 2 h and 30 per cent after 24 h. About 25 per cent Assam coal was extracted in AO after 2 h. Assam coal was used for these studies as this is a premium grade coal most suitable for solvent refining.

In order to reduce the extraction time, a stepwise extraction technique was developed by using AO, Qn and LP solvents in succession but on different sequences of 2 h extraction each^{16,17}. Assam coal was first extracted for 2 h in AO (25%), the residual coal was then subjected to Qn extraction for 2 h (20%) and the residual coal obtained from here, was further extracted for 2 h with LP (15%). Thus, overall 55 per cent Assam coal was rendered extractable in 6 h extraction time. Since out of these solvents, Qn was the most expensive (though coal derived), its use was eliminated which also reduced extraction time to 4 h. This resulted in extraction of 42 per cent Assam coal in AO-LP solvents after 4 h total extraction time.

In order to test the process of stepwise organosolvo-refining of coals on coals being currently used in thermal power stations, two coal samples were collected from two different local thermal power stations. These coals contained 28 per cent and 32 per cent MM contents respectively. The volatile matter in these coals was 26 per cent and 17 per cent respectively. These coals were tested for the AO-LP successive extraction of 2 h each step in a batch extractor. This resulted in the extraction of upwards of 35 per cent of coal. The residual coals obtained were found to be mostly fire as these contained more than 20 per cent volatile matter^{18,42-46}. The super-clean coal was recovered after distilling off the solvent from the extract.

The use of coal derived solvent such as anthracene oil in the extraction of coal is not new, however, the novelty of the process laid in the stage-wise successive sequential extraction of coal in the same solvent, i.e. AO or in different solvents. This research work was innovative as here the principles of cosolvency, solvent diffusion based disaggregation of coal macromolecules from coal particles by different solvents were exploited in successive solvent treatments and extractions.

Scaleup Studies using Semicontinuous Process

Extraction studies were carried out using 50 g to 500 g Assam coal in a batch extractor and the extraction results were found to be almost the same in the larger scales as obtained in smaller scale.

A vertical tubular trickle bed flow-through extractor of glass was designed and fabricated to handle and process 1/2 kg of Assam coal sample. The

extractor was heated electrically from outside^{18,41}. Extractions above 35 per cent were obtained by semicontinuous extraction process using anthracene oil. The AO was recycled as such in one operation and in another processing mode, AO was distilled and then recycled. The use of distilled AO showed better extraction results.

The advantage of semicontinuous extractor was that a large quantity of coal can be fed and in this case no separate filtration operation is required. The unextracted portion of solvent swollen coal is always in contact with solvent which trickles and flows through the coal bed. Thus, mass transfer of solvent to coal is facilitated and solvent is enriched with the organic matter from coal by breaking organic-inorganic matter affinity. This helps in reducing the extraction times up to 2-4 h.

The solvent refined coal obtained was almost a zero ash super-clean coal (SCC) and had high heating value. This had good flammability characteristics because of its high volatile matter contents. The recyclability of AO solvent was also studied and it was established that the solvent can be recycled and reused.

The residual coals obtained after solvent refining were found to retain sufficient volatile matter (> 20%) to render these coals flammable and fry.

These coals were also found to be free flowing and thus were suitable for firing in recirculatory fluidized bed combustors or for pressurised fluidized bed combustors¹⁸.

Thus, these studies have resulted in the development of an advanced, convenient, efficient and relatively cost-effective process for the organosolvo-refining of low grade Indian coals to get an environmentally clean fuel with high heating value. Fig.1 shows the flow-scheme of the process which is self-explanatory. In order to reduce the requirement of solvent, the coal may be cleaned by physical beneficiation techniques such as froth flotation, oil agglomeration or oleoflotation, etc. before feeding this to the extractor. The extraction timings can be varied as per the requirement of the depth of extractions up to 70 per cent. For larger extraction yields up to 95 per cent, several chemical pretreatments such as ATC³ (Alkylation-Transalkylation-Dealkylation - Degradation - Dehydrogenation) or depolymerization by phenolation, etc. reactions which employ coal derived solvents mostly can be used^{20,38,40}. Extensive research work on such pretreatments has been accomplished in author's laboratory^{14,20-23,25-35,38-40} and these pretreatments have been economised for use in the organosolvo-refining of coals and thus can be used if required.

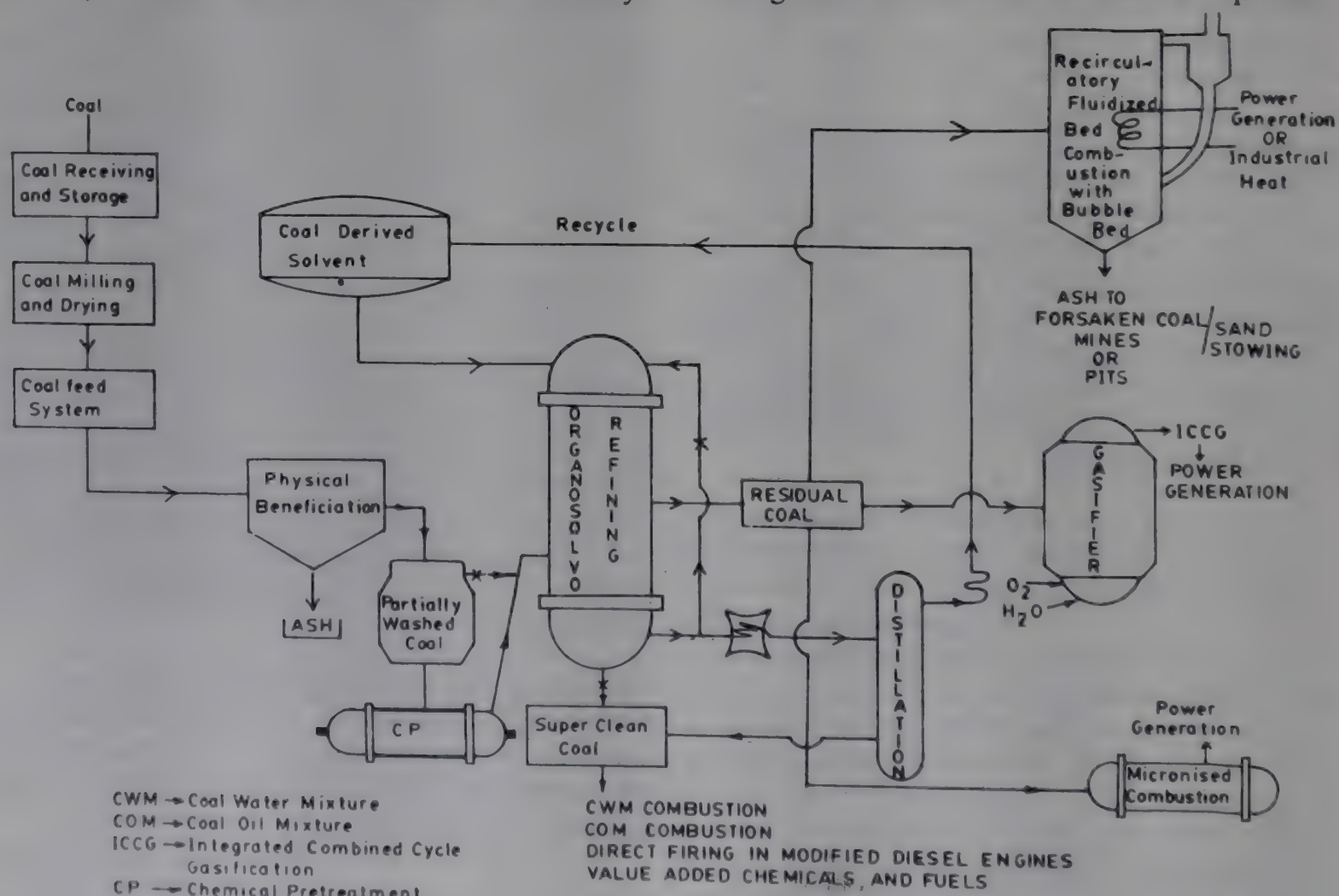


Fig. 1 Flow-Scheme of the process of Organosolvo-Refining of coal to get super clean-coal

The novelty of the present process lies in the recovery of reasonable amount (upwards of 35%) of premium organic matter from coal as a super-clean fuel with almost zero ash and with higher calorific value. The process is based on a theoretical insight into the nature of bonding of the mineral matter through chelates/coordination complexes/ligands at sites in the coal particle which carries 'ionic centres', aromatic-heterocyclic clusters with electronic and ionic sponges. The disintegration and disaggregation of MM from the organic coal matrix is a handiwork of polarity and solubilising power of organic lexiants having affinities for the organic coal matrix of low grade coals. The present process of organosolvo-refining of coals has been termed as SCC-IIT process.

Potential Uses of the Present (SCC-IIT) Process in Industries

This process transforms the coal into an environmental friendly source of energy and chemical feedstock. While in the classical physical cleaning process, a spread of the mineral matter is obtained between partially cleaned coal, middlings and rejects. The total ash emitted into the environment when all these are utilized remains same. Moreover, these processes produce at best only a partially cleaned coal as a substantial portion of the MM still remains with coal even after repeated washings. The levels of pollutants in the environment have reached high proportions and the ecological compulsions urgently warrant the search for advanced novel and effective methods which will hold back the MM from being discharged into atmosphere during combustion or by other modes of utilization. In the present process, the organosolvo-refining can be performed at the pitheads, the super-clean coal can be transported. This will reduce drastically the transportation costs. The residual coal can be fired at the nearby site, so that the ash obtained can be used in filling up the forsaken mines or pits or for sand stowing in mines.

The studies have been carried out to investigate the combustion, carbonization, gasification and washability characteristics of the residual coals obtained after organosolvo-refining of low grades coals^{18,41,42}. Kinetic studies^{16,17} on solvent extraction of coals have suggested that up to 70 per cent of coal can be extracted by using successive extraction with AO alone or in combination with LP and Qn in successive sequential extraction mode. The depth of extraction can be fixed as per the requirements of the process by varying the extraction timings^{16,17}. The residual coals obtained after

solvent refining were found to show good processability for gasification^{42,47}, carbonization⁴⁸ and combustion⁴³ of coal. Removal of organic matter would also render the physical or further chemical leaching of MM from the residual coal easier and convenient. Studies in this direction are currently underway.

Since the particle size of the coals is reduced after extraction of substantial amount of organic matter from coal, the residual coal may be fit for micronised combustion of coal for power generation at smaller scales. Residual coals were found to show good reactivity for steam gasification^{42,47}. Thus, these coals can be used for integrated coal gasification combined cycle power generation. In fact, as the present thermal power stations are ageing and may become redundant after 5-15 years after the completion of their designed life. Thereafter, following the recommendations of the Technology Information, Forecasting and Assessment Council (TIFAC)⁷ coal beneficiation plants for power generation on the basis of the SCC-IIT process may be set up. The residual coal may be utilized for: (i) recirculatory fluidized bed combustion, (ii) micronised combustion, and for combined cycle power generation. A beginning has already been made by using natural gas through H-B-J pipeline for combined cycle power generation in India. The natural gas may be depleted in India after 15-20 years, then these plants can be totally switched over to the gasification of coal.

Technology Transfer to User Industries

The process development work on the organosolvo-refining of low grade coals by using several other solvents which are already being used by coal and petroleum industries is in progress. Based on this innovative work a patent is being filed⁴⁹. This advanced process of refining of coal has a great potential for being further developed to be commercially exploited by the Indian industries while facing the oil crisis.

In fact, organosolvo-refining process constitutes a breakthrough in opening up newer avenues for coal utilization. Super-clean coal may be easily utilized in coal-water mixture or coal-oil-mixture combustion. This may also be directly used as a fuel in modified diesel engines. Some tests in this direction have been carried out at IIT, Delhi, and elsewhere^{50,51}. Beneficiated coal is also needed for solving the grave engineering problems due to the MM of coal in liquefaction, gasification and carbonization of coals (in steel plants and in low and medium temperature carbonization plants).

The super-clean coal can be easily processed to get value-added fuels and chemicals. The detoxified coal, free of toxic metals and corrosive alpha quartz would form a good boiler fuel in industries to replace the use of depletable oil and natural gas.

The downstream applications of the refined coal would include its use in aluminium industries as calcined petroleum coke (which is scarce) after blending with petroleum green coke.

The refined coal can also be blended with noncoking coals to yield coking coals for metallurgical industries.

Amongst other value-added uses for the refined coal, the likely suitability for use as feedstocks for carbon blocks and graphite electrodes for the electro-chemical industries would be important. This can also be used as carbon filler for rubbers and plastics.

Lastly the solvent refined coal can be readily hydrocracked to get oil. It is feasible to hydrocrack an extract unlike a solid coal in the presence of inorganic catalyst.

The process of organosolvo-refining of coal has been developed up to a 1/2 kg bench scale level. Further developmental work in the direction of process engineering is currently underway. Several novel extractors such as spinning basket extractor, recirculatory multifeed-counter current flow-through extractor, and fluidized bed extractor are being designed and fabricated for use in author's laboratory. We wish to invite the user industries for being involved in the further development in the process engineering work of this novel and advanced process of coal cleaning up to pilot plant and demonstration plant scale. After the transfer of the information about the present technology, the interested industries may come forward to adapt, use and further industrially develop this technology to suit their requirements. The development of the process and release of information to industry through present paper is a step towards the technology transfer to user industries by IIT, Delhi. The process may fit the recommendations of TIFAC⁷. It is suggested that coal refineries on the basis of SCC-IIT process may be set up in the coal utilizing industries after further development of the process. The environmental advantages of using (detoxified) clean coal may outweigh the economic considerations in the long run.

Technical and Economical Advantages of the Process

Realising the fact that indigenous oil reserves are not going to last for more than 15-20 years at the present rate of consumption and the rate of consumption is increasing rapidly. India is meeting

only 35 per cent of its oil requirement by the import of oil and already it is under enormous strain due to the pressure on foreign exchange reserves. The day is not far off when India may have to import the bulk of the oil required. It would be better to substitute the use of oil by coal. Since Indian coals are of low grade, therefore, organosolvo-refining (SCC-IIT) process may be adopted to get super-clean coal. A drive may be started to test the use of super-clean coal in industrial operations. Extensive trials have been made to use pulverized coal as a fuel in diesel engines⁵⁰⁻⁵². The super-clean coal can also be used for Coal-water-mixtures or Coal-oil-mixture combustion, and for micronised combustion etc. as discussed earlier.

The organosolvo-refining process involves the use of inexpensive coal derived solvents. It avoids the inconvenient industrial operations such as the use of hydrogen, and of high pressure and of separate filtration of viscous coal-extract slurries, etc. The design of the process is simple and it does not involve the use of costly material of construction of extractors, etc. as the whole operation is carried out under ambient pressure conditions. The solvents can be recovered, and recycled without their significant loss.

There is wide scope for varying the completeness of extraction as per requirements from 35 to 95 per cent. There are interesting and attractive options available for the use of the residual coals obtained after the extraction of the premium grade super-clean fuel from the coal feed. This invention of the process of organosolvo-refining of coal is being patented and application for the same has been submitted to IIT, Delhi⁴⁹.

The substitution of oil by Super-clean coal may have great potential to solve the grave problem of fuel requirement of Indian industries in twenty first century. The use of (detoxified) super-clean coal may also solve the environmental problems which are threatening the existence of life on this earth. Therefore, a beginning may be made by setting up coal refineries. In fact, low-grade Indian coals do not require just physical beneficiation but also super-refining for their efficient, convenient and cleaner utilization.

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Imidazoline derivatives as corrosion inhibitors

D A Raval and V M Mannari

Department of Industrial Chemistry, V P & RPTP Science College, Vallabh Vidyanagar, Gujarat 388120

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1,2-Disubstituted imidazoline derivatives were prepared from reaction between an aliphatic polyamine and different carboxylic acids. The products were tested for their corrosion inhibition efficiency on mild steel at varying concentration in 15% hydrochloric acid bath. For each inhibitor compound, the optimum concentration required is worked out. The study reveals that these products can successfully be used as acid corrosion inhibitor for mild steel.

Corrosion of steel is one of the most serious problems in chemical technology, both from technical and economic point of view. It has been estimated that in India more than Rs 200 crores worth of steel is lost because of corrosion every year.

Corrosion inhibitors have been in use since several hundred years and number of materials, either natural products, proprietary compounds or individual chemical species are used as inhibitors¹.

Imidazolines are one of the most important groups of inhibitors. Substituted imidazolines derived from condensation of polyethylene-polyamines and carboxylic acids (mainly fatty acids) have been synthesized and studied for their inhibition properties²⁻⁵.

In the present work, substituted imidazoline derivatives have been prepared from different polyethylenepolyamines and lower carboxylic acids as well as fatty acids derived from nontraditional oils. The imidazoline compounds were tested for their inhibition efficiency on mild-steel at different concentrations in 15% hydrochloric acid bath at room temperature.

Materials

Acetic acid, propionic acid and oleic acid (Laboratory reagent grade) were procured from reputed manufacturers. Argemone oil fatty acids and pilu oil fatty acids were prepared from respective oils (Purchased locally) and characterised.

Diethylenetriamine (DETA) was procured from the manufacturer M/s Diamines and Chemical Ltd, Baroda.

Mild steel pannels (5' × 5' × 0.1 cm) were used for corrosion study.

Experimental Procedure

Preparation of imidazoline compounds—Carboxylic acid (0.5 mol) and polyethylenepolyamine (0.5 mol) were condensed together in a 250 ml 3-necked round bottom flask, attached with a mechanical stirrer and a Dean and Stark assembly. Xylene (10% based on total charge) was added to the reactant mixture as a solvent for azeotropic distillation. The reactants were heated, under efficient stirring, to 120°C for 1.0 h. The temperature was then raised to 200°C and maintained between 200°-230°C until the completion of reaction. The progress of reaction was monitored by determination of acid value and amine value of sample at regular interval. After completion of the reaction, xylene was distilled off from the flask. The composition of different imidazoline compounds prepared for the acid corrosion inhibition study have been shown in Table 1.

Testing of imidazoline compounds for their inhibition efficiency—The inhibition efficiencies of different compounds in 15% (by wt) hydrochloric acid solution were tested by weight loss method. A series of acid baths having varying inhibitor concentration were prepared by dissolving required quantity of the compound in water and

Table 1 – Composition of various imidazoline compounds

Product code	Carboxylic acid	Amine
AD	Acetic acid	DETA
PrD	Propionic acid	DETA
OD	Oleic acid	DETA
ArD	Argemone oil fatty acids	DETA
PD	Pilu fat fatty acids	DETA

then adding the solution to acid baths. Mild steel coupons ($5' \times 5' \times 0.1$ cm) used for the experiment were thoroughly cleaned prior to their immersion by removing oil and grease, followed by rubbing with emery paper (No. 100) to obtain a smooth bright surface. Each coupon was weighed prior to its immersion in acid baths.

Mild steel coupons were then placed vertically in each bath, in such a way that they immersed completely, and were allowed to remain in the bath, at room temperature, for 24 h. The coupons were then taken out, washed with water, wiped, dried and accurately weighed.

Percentage inhibition efficiency E is calculated by the formula:

$$\%E = \frac{100(W_0 - W_i)}{W_0}$$

Where, W_0 = Weight loss of uninhibited coupon
 W_i = Weight loss of inhibited coupon

The results of the experiments for different compounds in 15% hydrochloric acid bath have been repeated in Table 2.

Results and Discussion

The results shown in Table 2 clearly indicate that all the imidazoline compounds prepared for the study show certain degree of corrosion inhibition of mild steel in hydrochloric acid solution at room temperature. Further, it also shows that at a given time for any given inhibitor compound, the percentage inhibition efficiency E increases with increase in concentration. However, the rate of increase of per cent inhibition efficiency is very low beyond certain value of inhibitor concentration. This indicates that for each inhibitor compound there exists a minimum level of inhibitor concentration corresponding to optimum per cent inhibition. Further, the study reveals that chain length of carboxylic acid has no significant effect on the inhibition efficiency of the compound. However, the chain length has controlling effect on the solubility of compound in different solvents. The amount of unsaturation in the fatty acid chain has no significant effect on the inhibition efficiency.

Table 2—Inhibition efficiencies (E) of various imidazoline compounds at different concentration on mild-steel in 15% HCl bath at room temperature

Inhibitor compound	Inhibitor concentration %	E % inhibition
Uninhibited	0.0	00.0
AD	0.1	64.0
	0.2	91.0
	0.3	96.2
	0.4	96.6
PrD	0.1	93.2
	0.2	95.2
	0.3	96.3
	0.4	98.0
OD	0.1	74.4
	0.2	84.0
	0.3	84.3
	0.4	87.9
ArD	0.1	89.9
	0.2	93.4
	0.3	94.1
	0.4	94.1
PD	0.1	92.3
	0.2	96.2
	0.3	96.5
	0.4	96.8

Conclusion

The imidazoline derivatives prepared in the study can successfully be used as corrosion inhibitors in hydrochloric acid baths. Commercially they can be used as additives to acid pickling baths to prevent steel losses.

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Corrosion in cracking processes and a measure for its control

Safaa T Keera, Elham A Eissa & Afaf R Taman
Egyptian Petroleum Research Institute, Nasr City, Cairo

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Corrosion of low carbon steel in various atmospheres (oxygen, air, H_2S and SO_2) at different temperatures was studied. Sodium sulphate oxidizes the carbon steel more than oxygen and H_2S .

Effect of artificial ash ($Na_2SO_4:V_2O_5$) in a ratio of 1:3 was studied on steel and copper metals. It was thermally analyzed by thermoanalytical techniques—Vanadium and sodium react to form products which melt at $526^\circ C$ (NaV_3O_8), it is the most corrosive in residual fuels.

Hot ash corrosion of the two metals was studied at 600° , 700° and $800^\circ C$. The corrosion rate of the two metals increases with increasing temperatures.

Effect of adding MgO as inhibitor at various concentrations was studied.

Cracking is the most significant process in petroleum refining¹. It improves the feed by reducing the concentrations of polycyclic aromatics and sulphur compounds², the nitrogen content and Conradson carbon are also reduced³.

Vanadium, sodium and sulphur compounds are the most important impurities in crude oil. They lead to the formation of aggressive materials towards metallic surfaces at high temperatures in catalytic, hydrotreating and desulphurization process.

Experimental Procedure

Ashing of Gysume crude oil

The residue over $450^\circ C$ produced by atmospheric and vacuum distillation of Gysume crude oil, was converted by gradual heating to a final temperature 750° with concentrated sulphuric acid.

Analysis by atomic absorption techniques

The ash obtained from Gysume crude oil was analyzed using atomic absorption technique⁴. The sample under test exposed to microprobe analysis model JEOL, JSM200 at magnification 50, and the time analysis 100 second.

Thermal analysis

The artificial ash was prepared by mixing and grinding sodium sulphate and vanadium pentoxide at 1:3 ratio by weight in a mortar for 20-30 min. 10 mg of the tested as sample was introduced into DTA pan and placed in the head assembly, where

a reference pan, containing alumina, was also placed. The heating rate was $10^\circ C/min$ with the chart speed 5 mm/min. The recorder displayed the thermal changes occurring to the sample, producing the corresponding DTA curve, from which the onset maximum peak temperature were measured.

Effect of various atmospheres on oxidation of carbon steel

The carbon steel specimens containing 0.15% C were exposed to various atmospheres (oxygen, air, H_2 and in presence of Na_2SO_4) for a period of 24 hr in a furnace at different temperatures 500° - $900^\circ C$ the weight loss in mg at each temperature were measured.

Corrosion was measured using weight loss method

Mixture of artificial ash with magnesium oxide was prepared to have 1:2, 1:1 and 2:1 by weight.

Method

The cleaned carbon steel and copper specimens were coated with ash obtained from Gysume crude oil, artificial ash and its mixtures with MgO to attain a coating of about 20 mg/cm^2 . The specimens were placed in a muffle furnace together with a blank specimen and heated for 7 hr at 600° , 700° and $800^\circ C$.

Finally, the specimens were weighted to determine loss in weight after dipping in caustic soda solution containing zinc dust at $60^\circ C$ for 5 min., washing with tap water, distilled water, drying and rinsed with benzene⁵.

Results and discussion

Analysis of ash content by atomic absorption

The analysis indicated that the ash obtained of Gysume crude oil contained a considerable number of elements as shown in Table 1. Fe, Ni and V are found in highest concentrations followed by $Zn > Cu > Co$.

Effect of various atmosphere on corrosion of carbon steel

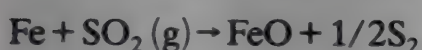
Fig. 1 illustrates the effect of various atmospheres on the rate of oxidation of carbon steel specimen for exposure periods of 24 hr (500°-900°C and it is found that in Fig 1 oxygen and air oxidize the c-steel at about the same rate. Sodium sulphate has higher effect.

It is evident that in presence of oxygen atmosphere FeO is formed mainly by cationic diffusion into vacancies at the oxide gas interface. The anionic lattice grows by adsorption of further O^{2+} anions. The Fe_3O_4 is also produced by cationic diffusion on the top of FeO, but the thin layer of Fe_3O_4 which is produced at the outer surface of the oxide is formed by anionic diffusion⁶.

Hot corrosion of steel in presence of Na_2SO_4 has considerable interest⁷. Na_2SO_4 decomposes into SO_2 and SO_3 .



In the initial reaction of SO_2 with clean metal, oxide is almost the primary product.



The S_2 formed during the reaction is also incorporated into the anion lattice and this is able to diffuse towards the oxide-metal interface. A new metal sulphide is produced between the oxide and the metal which continues to grow by the inward migration of sulphure anions to the metals⁸. The presence of Na_2SO_4 retard the inwards diffusion of sulphur anions.

Effect of hydrogen sulphide on corrosion of carbon steel

Fig. 1 indicates that the rate of corrosion of carbon steel in presence of H_2S increases with increasing temperatures (500°-900°C). Hydrogen sulphide directly attacks the surface of the metal and reacts rapidly to form metal sulphide. It causes a reduction in strength by decreasing the effective wall thickness of equipment. This could be related to the nature of the scale formed, whereas the sulphide scales have more defects and

Table 1—Metal analysis in Gysume crude oil using atomic absorption technique

Elements in crude oil	Wt of element $\times 10^3$
Fe	10.52
Cu	0.45
Co	0.022
Zn	0.69
Ni	4.06
V	4.10

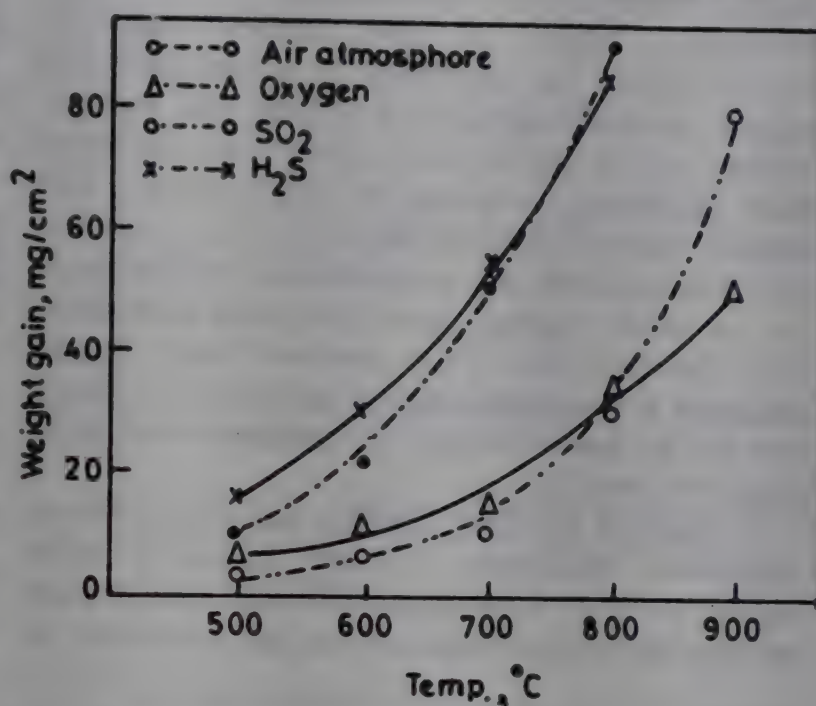


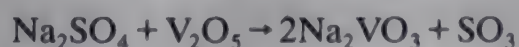
Fig. 1—Corrosion of c-steel (0.15 C%) in various atmosphere

cracking, thus enhancing the diffusion of H_2S . This is due to the wide variations in temperature during operation⁹.

Thermoanalytical technique on hot ash corrosion

Fig. 2 shows the TGA and DTA curves of the 1:3 mixture of (Na_2SO_4 and V_2O_5). It was found that the onset temperature occurs at 485°C. Two endothermic peaks at 500° and 650°C are interrupted by exothermic peaks at 550°C and at 720°C.

The two endothermic peaks represent the two stages in weight loss involved, 3 and 8.3 per cent respectively, the first referring to the melting point of the eutectic mixture. Vanadium and sodium react to form products melting at 526°C ($Na Va_3 O_8$) these low melting compounds are the most harmful corrosives in residual fuels. Investigation¹⁰ indicated that three compounds were formed by reaction of Na_2SO_4 and V_2O_5 .



The other endothermic peak is due to the evaporation of the products of the thermal breakdown (SO_3).

The two exothermic peaks may be due either to lower bond strength or to decomposition related to the specific nature of substituents.

Corrosion of carbon steel and copper at high temperatures

Figs (3 & 4) and Tables 2 & 3 illustrate the thermal treatment of sulphated ash produced from Gysume crude oil and artificial ash 3:1 ($\text{V}_2\text{O}_5:\text{Na}_2\text{SO}_4$) on corrosion of carbon steel and copper specimen surfaces. It is clear that the corrosion rate of carbon steel and copper increases with increasing temperatures ($600^\circ\text{--}800^\circ\text{C}$). The metallic scales appearing (NaV_3O_8) after the thermal treatment are dull grey or black and are present as brittle surface layers and lack adherence. The corrosion rate of ash obtained from Gysume crude oil is lower than that of artificial ash. This is due to the lower content of vanadium and presence of Ni and Zn.

In spite of fact that Na_2SO_4 has no individual aggressive behaviour towards metals¹¹, when added to V_2O_5 it facilitates the low temperature melting of the ash and initiates the formation of

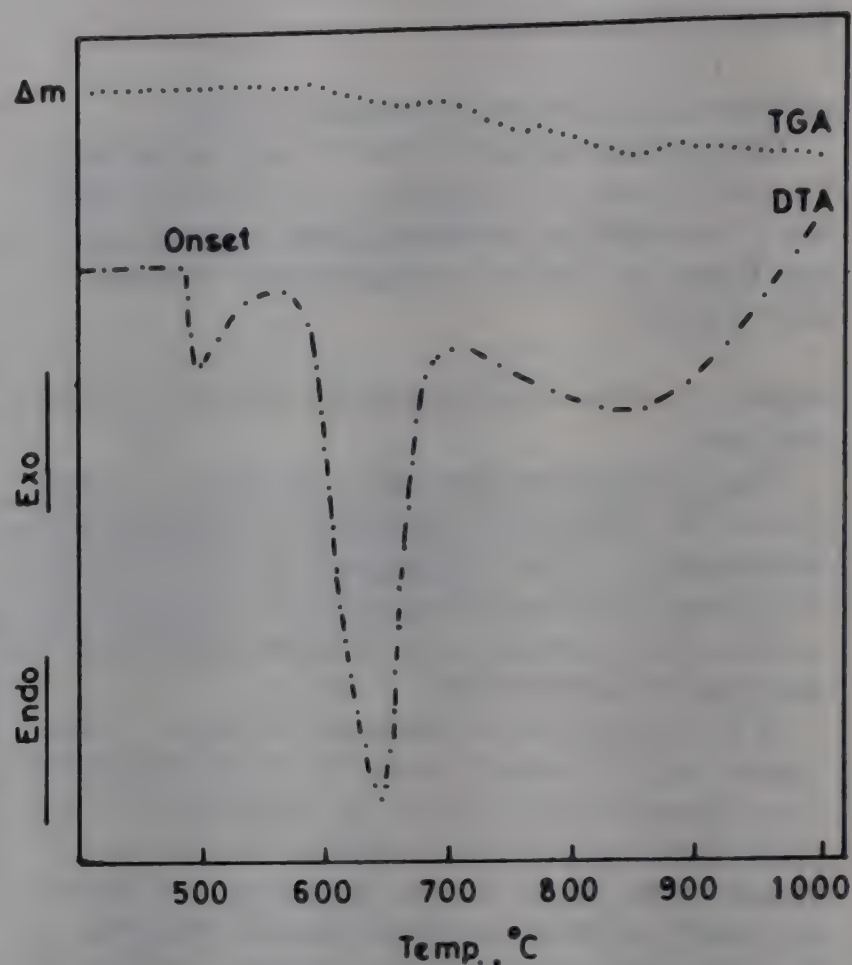


Fig. 2—TGA and DTA curves of the artificial ash ($\text{Na}_2\text{SO}_4:\text{V}_2\text{O}_5$, 1:3 by wt)

Table 2—Corrosion rate of c-steel and inhibition efficiency in the presence of magnesium oxide

MgO:Ash	Corrosion rate, mg/mc ² /hr			Inhibition efficiency %		
	600°C	700°C	800°C	600°C	700°C	800°C
Nil	0.182	0.206	0.730	—	—	—
0:1	0.552	20.00	30.590	—	—	—
1:2	0.123	2.50	7.540	77	87.5	75.4
1:1	0.100	1.28	0.543	81	93.6	98
2:1	0.090	1.40	0.690	83.7	94.8	97.7
Sulphated ash from crude oil	0.332	7.301	11.441	—	—	—

Table 3—Corrosion rate of copper and inhibition efficiency in the presence of magnesium oxide

MgO:Ash	Corrosion rate, mg/mc ² /hr			Inhibition efficiency %		
	600°C	700°C	800°C	600°C	700°C	800°C
Nil	0.129	0.564	0.742	—	—	—
0:1	0.456	8.984	27.82	—	—	—
1:2	0.0899	2.062	5.82	80.0	77.0	79.0
1:1	0.0811	1.331	0.645	82.0	85.2	97.7
2:1	0.0717	1.108	0.526	84.0	87.7	98.1
Sulphated ash from crude oil	0.258	7.509	10.452	—	—	—

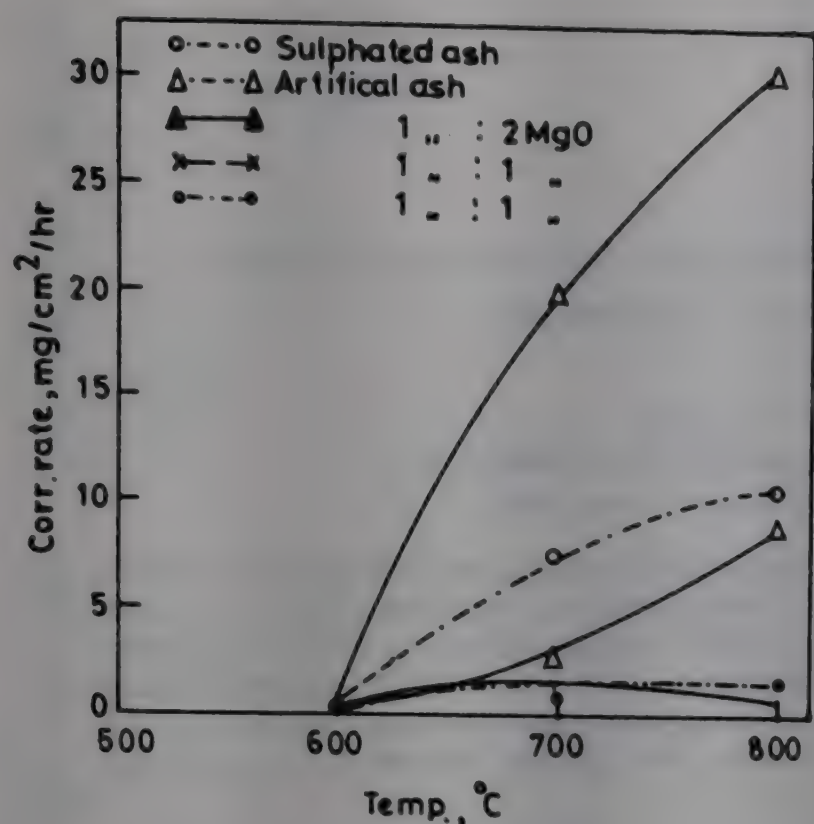


Fig. 3—Influence of adding various amounts of magnesium oxide on corrosion of c-steel in presence of ash

NaV_3O_8 which causes external corrosion in the metal surface. This is due to the fact that vanadium makes Na_2SO_4 and both form corrosion. Also, Na_2SO_4 can dissolve the initially formed protective oxide scale as a result of the departure from stoichiometry.

Effect of magnesium oxide as inhibitor

Figs 3 & 4 and Tables 2 & 3 indicate that the effect of addition of MgO to artificial ash with various ratios (MgO:Ash) 1:2, 1:1 and 2:1 respectively. It is noted that the rate of corrosion decreases with increasing MgO contents at all temperatures (600°-800°C). Vanadium attack has been minimized by the use of MgO, which reacts with the vanadium to form a high melting point magnesium vanadate which does not stick to the blade surface. The inhibitive efficiency is a function of the MgO content of the ash. At ratio 2:1 MgO:Ash has maximum corrosion inhibition. The addition of MgO is highly effective in protecting the two metals and reducing the weight loss.

The inhibitive efficiency increases with increasing temperature. This is due to the fact that higher temperature leads to faster consumption of V_2O_5 and MgO to give magnesium vanadate, $\text{Mg}_2\text{V}_2\text{O}_6$, which is further stabilized by the formation of $\text{Na}_2\text{V}_2\text{O}_7$ and improved the hot ash corrosion inhibition.

Conclusion

Sodium sulphate oxidizes the carbon steel more than oxygen and H_2S .

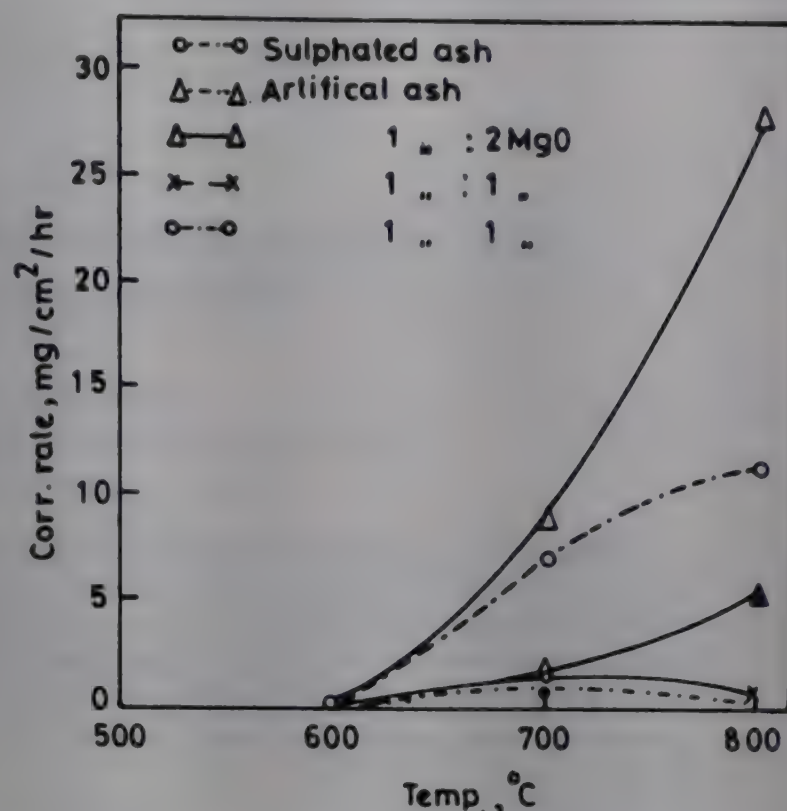


Fig. 4—Influence of adding various amounts of magnesium oxide on corrosion of copper in presence of ash

Vanadium and sodium react to form products which melt at 526°C (NaV_3O_8), it is the most corrosive in residual fuels.

The corrosion rate of the two metals increases with increasing temperatures.

The inhibitive efficiency of the two metals is a function of the MgO content of the ash and increased with increasing temperature.

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Effect of flyash addition on dielectric behaviour of glass reinforced polyester composites

Navin Chand & K K S Gautam

Regional Research Laboratory, Habibganj Naka Road, Bhopal 462 026

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Different amount of flyash particles with and without glass fibres were incorporated in the polyester resin. Role of addition of these particles with and without glass fibres on dielectric behaviour of polyester resin is investigated in the temperature range ranging from 26°C to 160°C. Changes occurred in dielectric behaviour due to incorporation of flyash particles and glass fibres are discussed. ϵ' values at 400 Hz frequency for A, B and C composites having 25.2, 16.8 and 8.4 gm of flyash along with glass fibres were 5.05, 5.05 and 4.5 respectively. Increase of flyash weight fraction has decreased the dielectric constant of the composite.

Large number of fibres are generally incorporated in epoxies, polyesters, phenolics, alkyds, PVC and in polyethylene^{1,2}. Recently we have developed composites of flyash and glass fibres with polyester resin and reported their structural and thermal properties³ in the previous paper. Incorporation of flyash improved thermal stability of composites³. Effect of flyash particle on wear loss behaviour was also reported by us recently. Dielectric behaviour of pure polyester and reinforced polyester resin is reported by several investigators⁴. But no report is available on dielectric behaviour of flyash-glass fibre reinforced-polyester composites.

In this study a waste filler, flyash, is incorporated in different sizes and weight fractions in polyester resin with and without glass fibres. Glass fibre's quantity was kept constant. Dielectric properties such as dielectric constant (ϵ') and dissipation factor ($\tan \delta$) of these composites were determined at different temperatures and are reported.

Materials and Methods

Composites of flyash with polyester resin with and without glass fibre were prepared by incorporating different size particle of flyash in various concentrations. General purpose polyester resin (unsaturated) supplied by MP Polymers, Bhopal, India was used. 2 per cent initiator and hardner each were mixed before mixing the flyash particles in the polyester resin. Mixed was poured with and without glass fibres into the steel moulds. After 24 hours composite sample was removed out of moulds and post cured at 80°C for 2 hours in oven.

Samples AF₁, AF₂, AF₃, AF₄, AF₅, A, B, C, D and E were the same reported in previous paper³.

Dielectric Measurements

ϵ' and $\tan \delta$ of the composites were determined by using a Hewlett Packard's LCR meter. 1 cm × 1 cm size samples were coated by air drying type conducting silver paint. Measurements were done by using brass electrodes cell in the temperature range ranging from 26°C to 160°C.

Results and Discussion

Previously it was observed that in corporation of flyash particles had reduced the tensile strength of pure polyester resin³. Figures 1 to 10 show the variation of dielectric constant (ϵ') and dissipation factor(D) of flyash polyester composites FA₁, FA₂, FA₃, FA₄, FA₅, A, B, C, D and E respectively. Increase of flyash loading has decreased the dielectric constant marginally. At 400 Hz, ϵ' of AF₁ and AF₂ are 5 and 5.1 respectively. On incorporation of glass fibres alongwith flyash particles, dielectric behaviour of composites got modified. ϵ' values for A, B and C were 5.05, 5.05 and 4.5 respectively. Figs 3 & 4 show that at all temperatures ϵ' value of AF₃ are less than AF₄. Dissipation factor for AF₄ at 400 Hz is higher as compared to AF₃.

Figs 6 and 7 show that ϵ' values for A and B samples were nearly same, this is due to glass fibres incorporation, which has increased ϵ' but reduced the difference. Increase of flyash particle size with glass fibres incorporation increases dielectric constant very little. ϵ' values of composites A, B and C increases with increase of temperature and attains a constant value after 110°C.

E glass has generally ϵ' value 6.13 at 10 kHz. Increase of flyash loading in flyash polyester

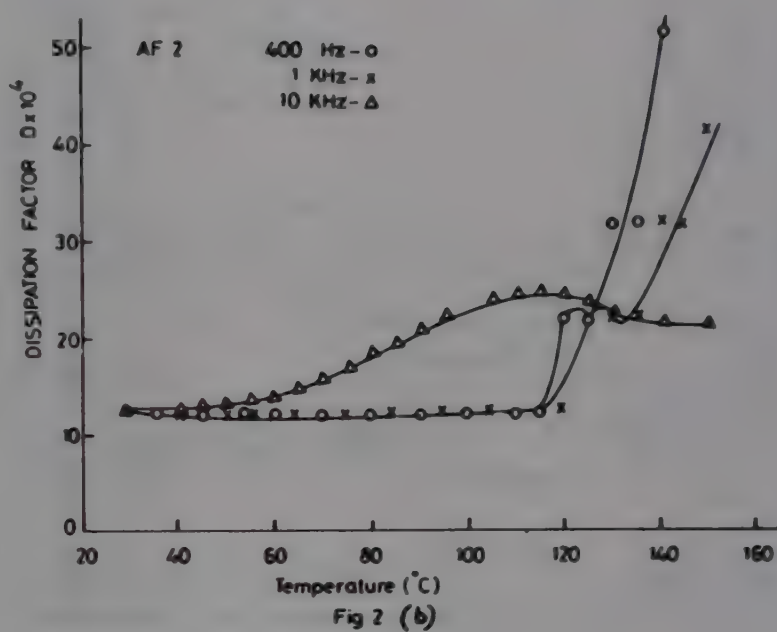
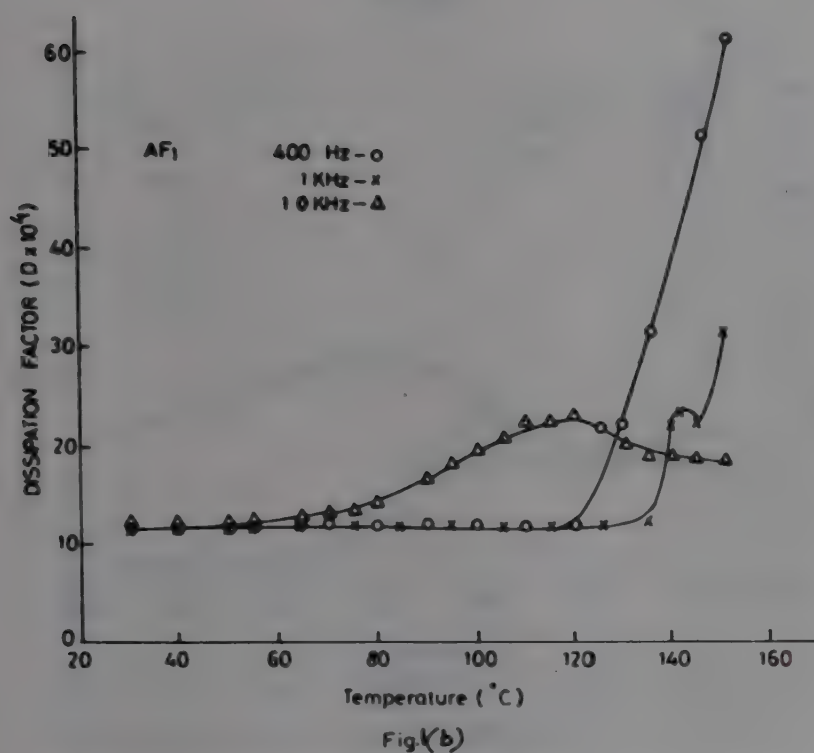
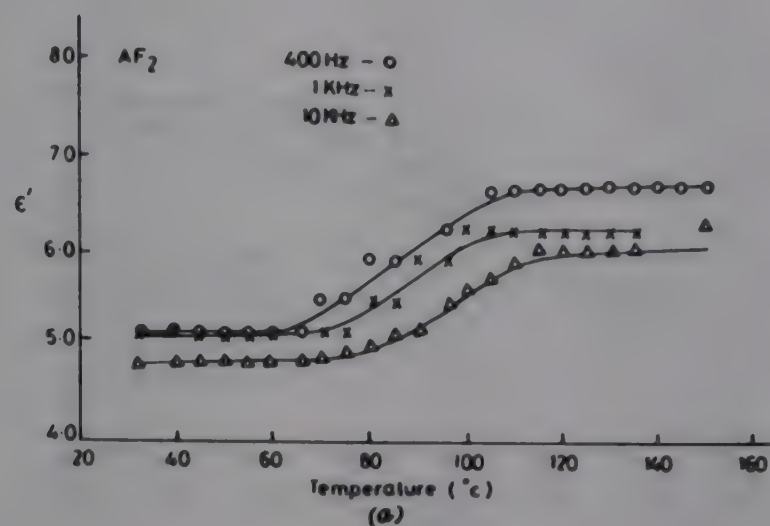
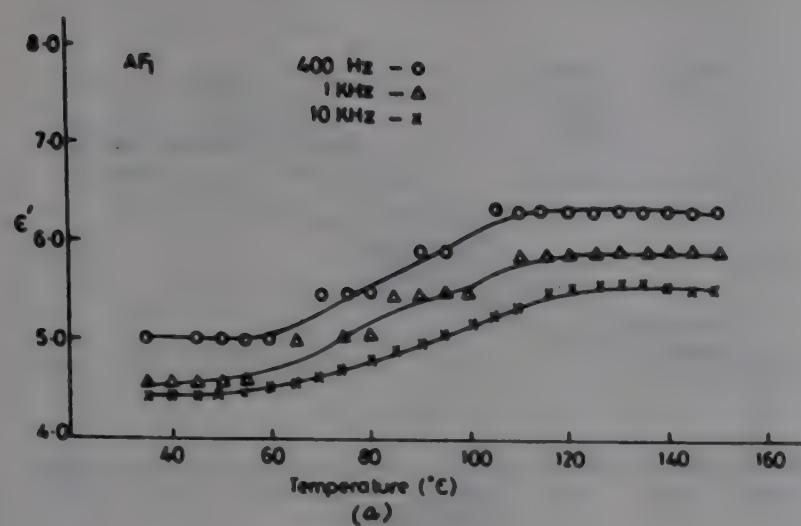


Fig. 1a, b— ϵ' and dissipation factor variation with temperature for AF_1 composite

Fig. 2a, b—Variation of ϵ' and dissipation factor with temperature for AF_2 sample

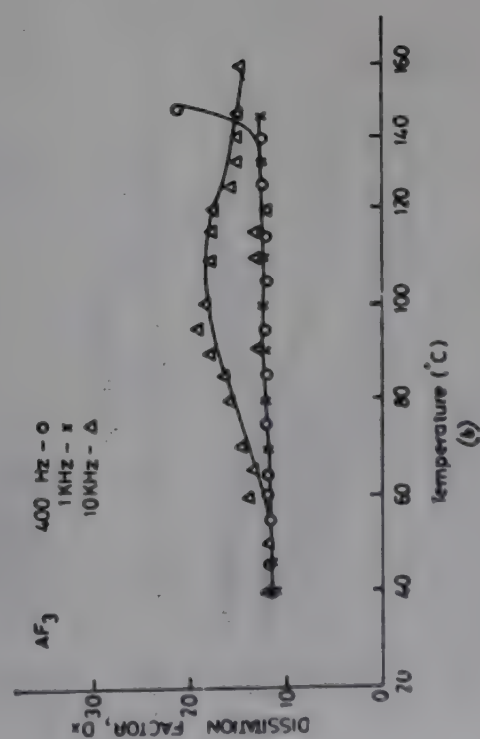
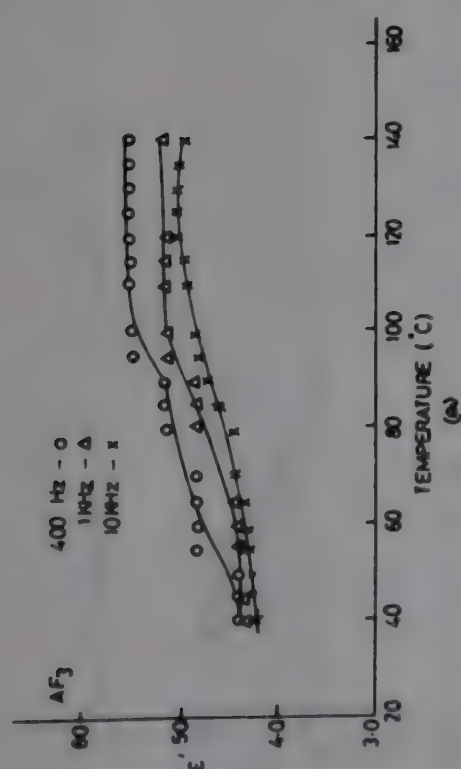


Fig. 3a, b—Dependence of ϵ' and dissipation factor on temperature for AF_3

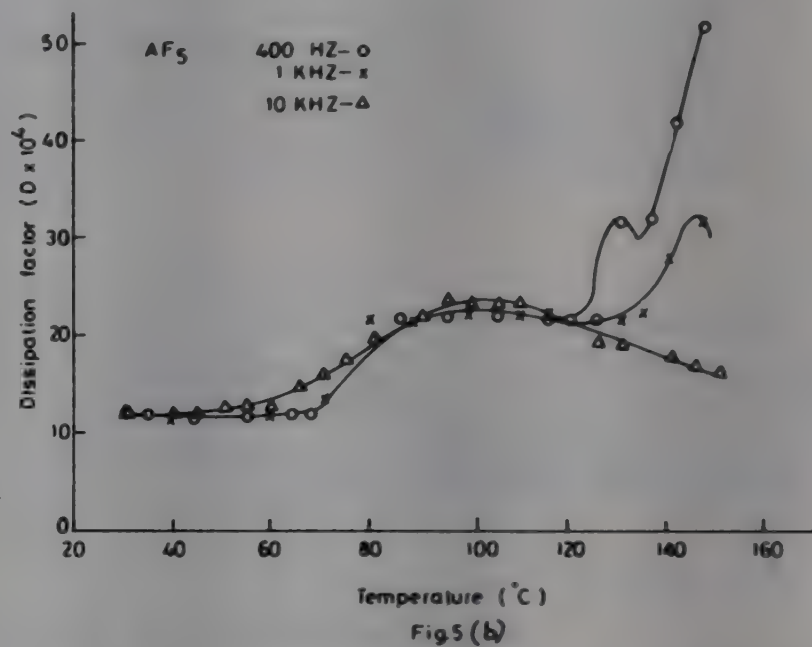
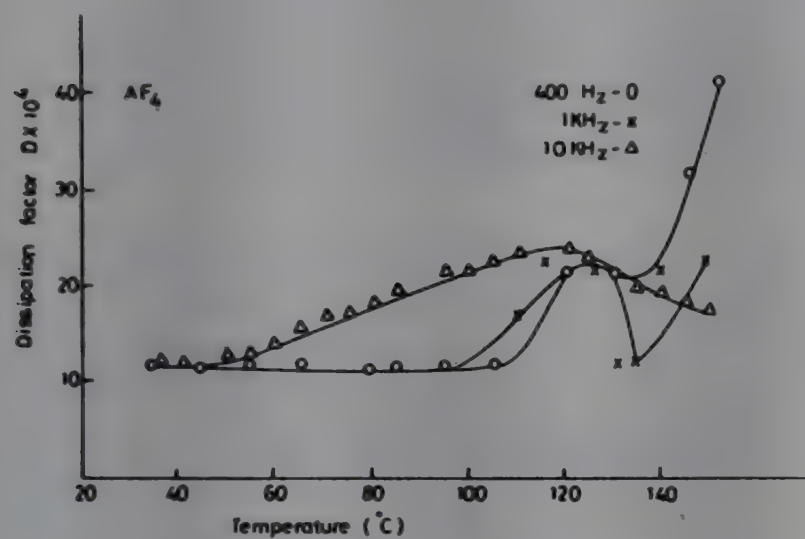
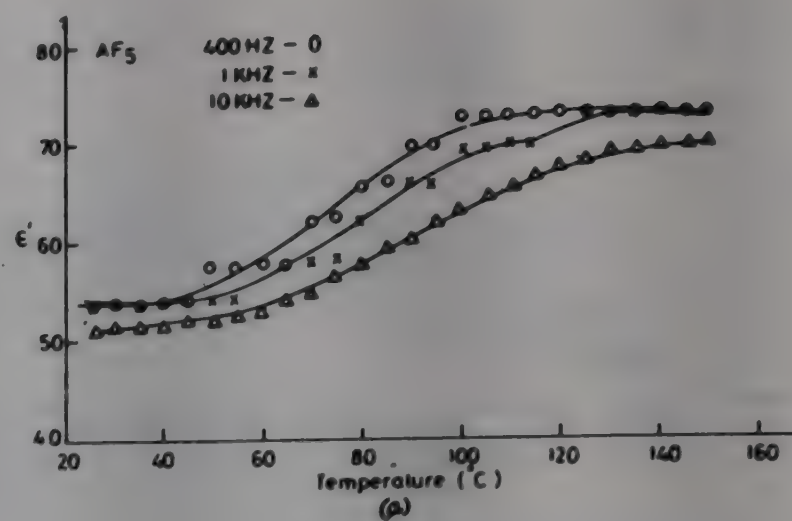
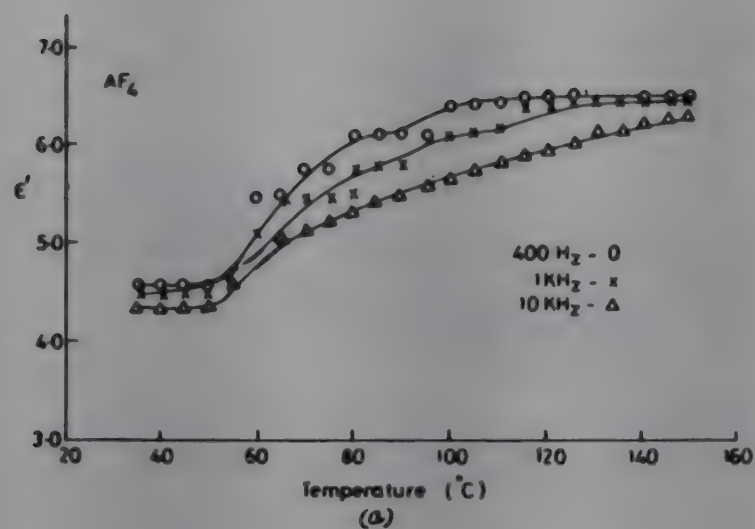
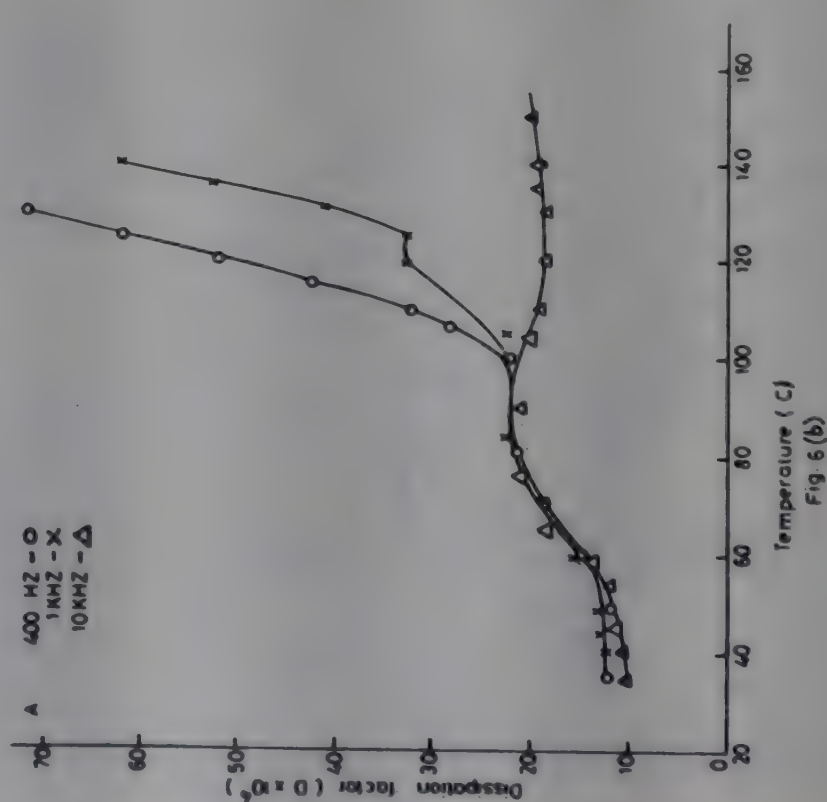
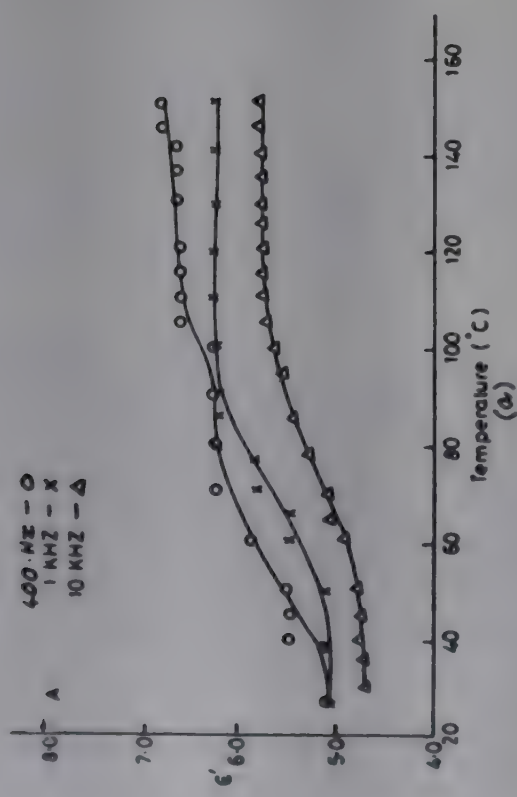


Fig 4(b)

Fig 5(b)

Fig. 4a, b— ϵ' and dissipation factor variation with temperatureFig. 5a, b— ϵ' and dissipation Vs temperature plot for AF₅ compositeFig. 6a, b—Variation of ϵ' and dissipation factor with temperature for composite A

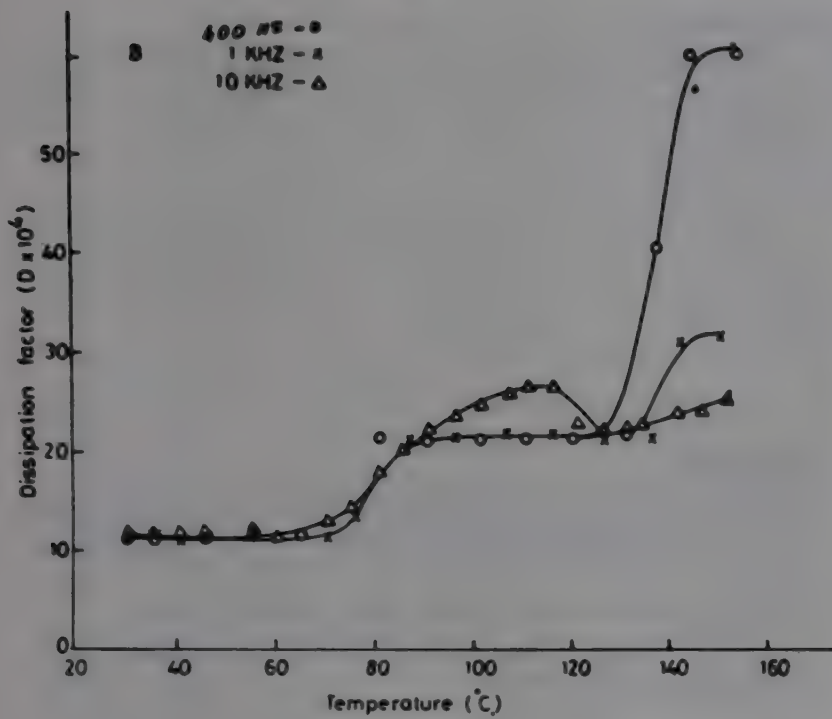
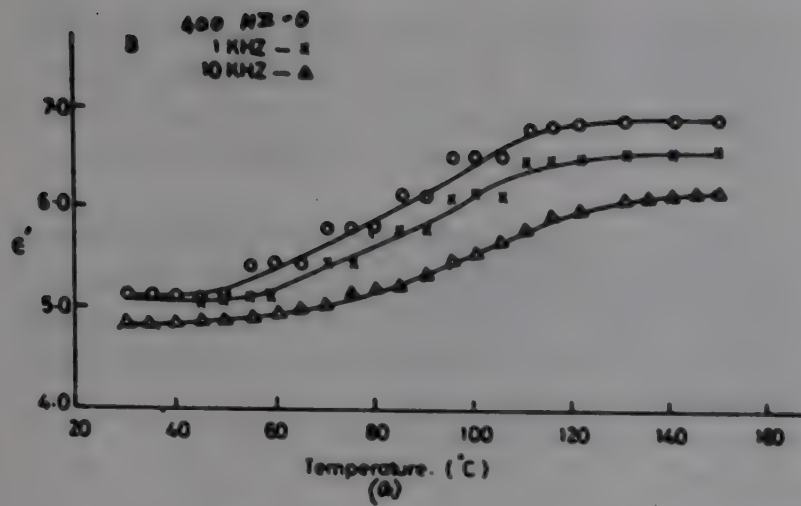


Fig. 7 (b)

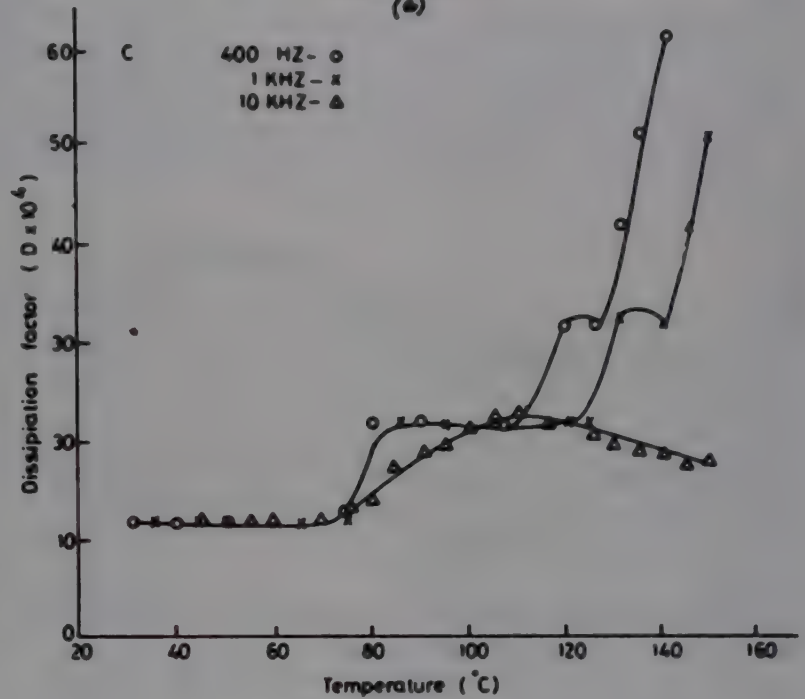
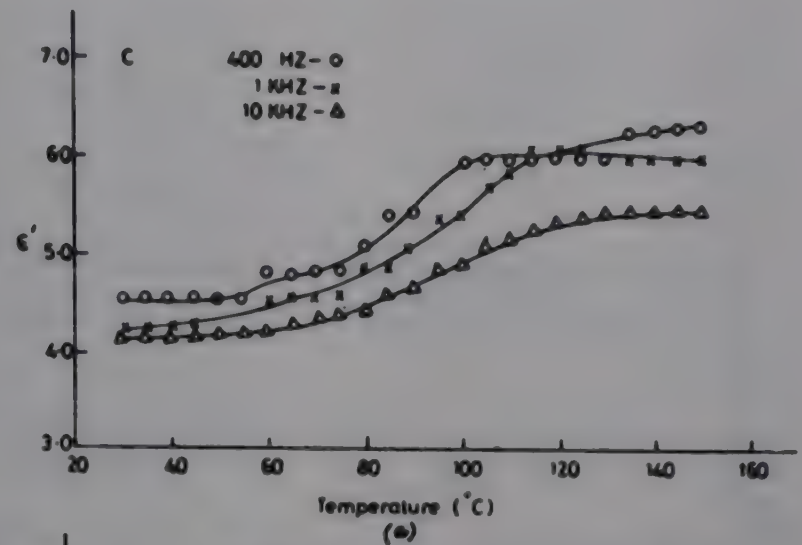
Fig. 7a, b—Change in ϵ' and dissipation factor with temperature for B

Fig. 8 (b)

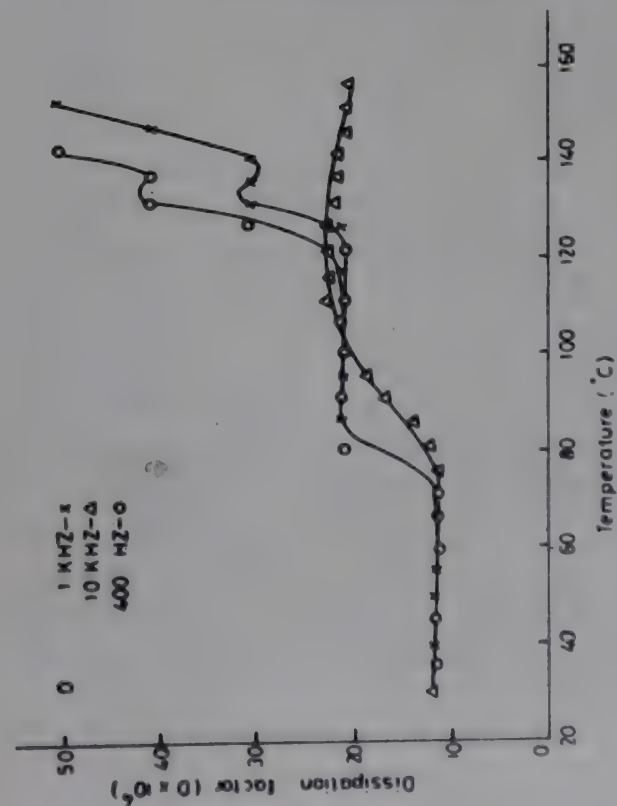
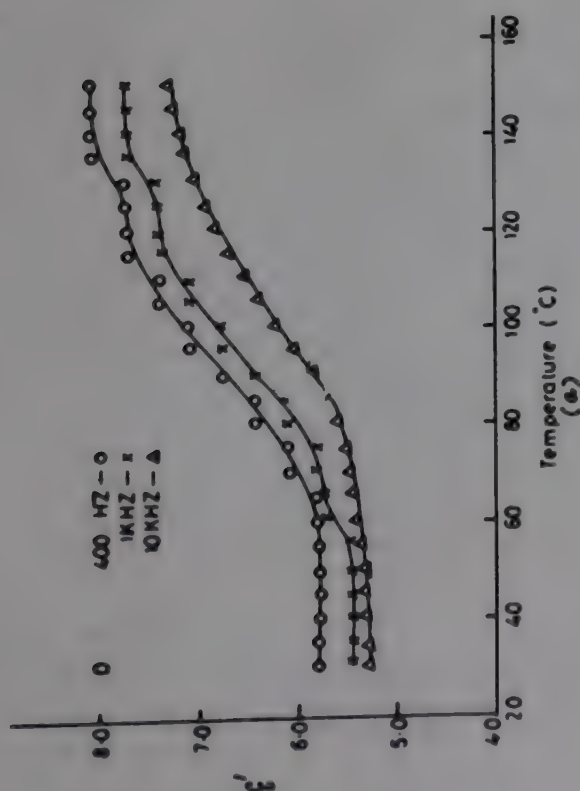
Fig. 8a, b—Dependence of ϵ' and dissipation factor on temperature for composite C

Fig. 9 (b)

Fig. 9a, b—Variation in ϵ' and dissipation factor with temperature for composite D

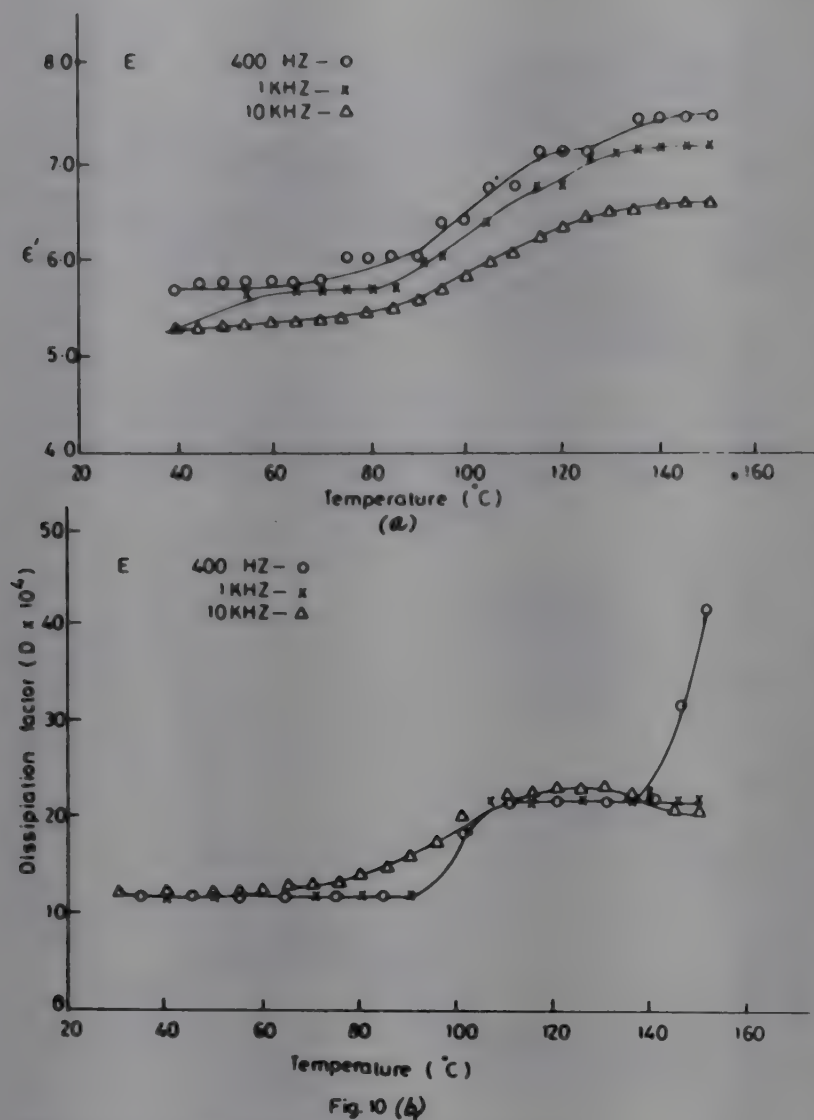


Fig. 10 (a)

Fig. 10a, b— ϵ' and dissipation factor dependence on temperature for composite E

composites shifted the $\tan \delta$ peak position to higher temperature side. In case of flyash-glass-polyester composites 400 Hz frequency second peak of $\tan \delta$ disappeared on increasing the flyash loading.

Size of flyash particle did not affect the $\tan \delta$ value in case of pure flyash-polyester composites. But in case of glass reinforced flyash-polyester composite decrease of flyash size shifted the $\tan \delta$ peak of 10 kHz to higher temperature side.

Conclusions

1. Flyash particles with and without glass fibres modify the dielectric constant values at all temperatures

2. Increase in temperature increases ϵ' value for A, B and C composites, which attains a constant value after 110°C.

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Production of cellulases and β -glucosidase by *Aspergillus oryzae* and enzymatic saccharification of some cellulosic wastes

Lalitagauri Ray & S K Majumdar

Department of Food Technology & Biochemical Engineering, Jadavpur University, Calcutta 700 032

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Aspergillus oryzae grown in solid state fermentation produces carboxy methyl cellulase, filter paper degrading enzyme, and β -glucosidase with optimum activity of each enzyme component at pH 4.8 and 60°C. The organism is found to be a rich source of β -glucosidase (12.59 IU/ml). Glucose inhibits the β -glucosidase activity. Cysteine has stimulatory effect on the activity of cellulase components. Treatment of 2 per cent rice straw (alkali-treated) with the mold culture filtrate at pH 4.8 and 60°C gives 59.85 per cent saccharification in 72 h.

Cellulose occurs in abundance in nature and constitutes one-third to one-half of the approximately 150 billion tons of organic materials that are photosynthesized annually¹. The commercial possibility of using cellulase preparations to produce glucose, alcohol and protein from cellulose is under intensive study²⁻³. Data for the commercial feasibility of the enzymatic hydrolysis of cellulose are based on laboratory or pilot plant study⁴⁻⁵. The major problems encountered are to obtain sufficiently active cellulase enzymes and suitable substrates so that high concentration of glucose can be obtained in a reasonable time period. Three different kinds of enzymes believed to be involved in cellulose decomposition are endo- β -1,4 glucanase, exo- β -1,4 glucanase and β -glucosidase⁶⁻⁹. Other enzymes may be involved in this process but definite evidence is lacking. For commercial enzymatic hydrolysis of cellulose to glucose, the production of exo- β -1,4 glucanase, endo- β -1,4 glucanase and β -glucosidase in high yields are essential. The present work reports on the production of cellulases, viz. carboxy methyl cellulase (CMCase), filter paper degrading activity (FPA), and β -glucosidase by *Aspergillus oryzae* and some of the characteristics of these enzymes and finally on the saccharification of some cellulosic wastes by *A. oryzae* culture filtrate.

Materials and Methods

Aspergillus oryzae used for the production of the enzymes was maintained on Czapek Dox agar medium (pH 4.8) at 4°C.

Production of enzyme — The enzymes were produced in solid state fermentation using sterile

wheat bran containing 50 per cent moisture. The production of the enzyme was studied for 7 days at different temperatures between 24°C and 35°C. For studying the characteristics of the enzymes, 85 ml of enzyme extract was prepared in distilled water from 25 gm ground mold bran¹⁰. The extract was then centrifuged at 4000 rpm to get the clear enzyme solution.

Enzyme assay — Carboxy methyl cellulase (CMCase) filter paper degrading activity (FPA) and β -glucosidase activity of the enzyme extract were measured following the standard methods. For CMCase assay an aliquot (1.0 ml) of suitably diluted enzyme solution was incubated with 10 mg of CMC in 1 ml 0.2 M acetate buffer (pH 4.8) at 60°C for 30 mins. For determination of filter paper -degrading activity, 1.0 ml diluted enzyme solution was incubated with 50 mg of filter paper (Whatman no.1) in 1.0 ml 0.2 M sodium acetate buffer (pH 4.8) for 1 h at 60°C. β -glucosidase activity was determined by incubating 1.0 ml suitably diluted enzyme solution with 1.0 ml (10 mg/ml) salicin solution in 0.2 M acetate buffer (pH 4.8) at 60°C for 30 mins. In each case reducing sugar produced was estimated by dinitrosalicylic acid method¹¹. Enzyme activity is expressed in international unit (IU) which is defined as μ mole of glucose liberated per min. per ml of enzyme solution under the assay condition.

Pretreatment of cellulosic wastes before saccharification — Cellulosic wastes like rice straw, bagasse, jute stick were cut into small pieces and then autoclaved with 1 N sodium hydroxide solution for 30 mins¹². Finally they were thoroughly washed until the materials were completely free from alkali. The materials thus obtained was oven-dried at 80°C overnight.

Saccharification of cellulosic wastes — Saccharification by enzyme extract was studied using alkali-treated (AT) and untreated (UT) cellulosic wastes as the substrate. Studies were made to find the effect of enzyme and substrate concentration on the saccharification at 24, 48 and 72 h of incubation. The reaction mixture (20 ml) containing 2 and 5 per cent substrate and different volumes of enzyme extract (pH 4.8) was taken in 50 ml Erlenmeyer flask which was then incubated at 60°C for 72 h. The amount of reducing sugar in the reaction mixture was estimated¹¹ at 24 h intervals.

Results

Enzyme production — The organism *Aspergillus oryzae* gives optimum yield of each cellulase component, viz. CMCase, FPA and β -glucosidase at $28 \pm 2^\circ\text{C}$ on the 5th day of fermentation. The particular temperature and the optimum day of fermentation were optimised in the laboratory.

Optimum pH and temperature for enzymatic hydrolysis — Hydrolysis of CMC, filter paper and salicin (for β -glucosidase activity) by *A. oryzae* cellulases were measured over a pH range of 4.0 to 5.5 and temperature range of 30°C to 80°C. The enzyme extract shows maximum CMCase (3.61 IU/ml), FPA (0.46 IU/ml) and β -glucosidase (12.59 IU/ml) activities at the same pH 4.8 and temperature 60°C (results are not shown). Q_{10} (45°-55°C) for CMCase, FPA and β -glucosidase were 2.35, 1.13 and 1.87.

Effect of substrate concentration — The effect of carboxy methyl cellulose on CMCase activity and of salicin on β -glucosidase activity were determined.

The K_m values of CMCase and β -glucosidase as calculated from Line weaver- Burk plot were 20 per cent and 16.6 M respectively. The V_{max} (μmole glucose released per min per ml of culture filtrate) for CMCase and β -glucosidase were 10.0 and 0.20 respectively.

Effect of glucose on β -glucosidase activity — Glucose was found to be inhibitory to the action of β -glucosidase (Fig.1). There was a rapid fall in enzymatic activity when glucose was added at a concentration of 2-4 mg/ml to the enzyme reaction system (0.24 IU of enzyme) and only 12 per cent of maximum activity was observed at glucose concentration of 10 mg/ml. Glucose inhibition of β -glucosidase activity of some fungi was also reported by a number of investigators¹³⁻¹⁵.

Effect of organic compounds on the activity of cellulases and β -glucosidase — Different organic compounds, e.g. EDTA, SDS, L-cysteine, ammonium thiocyanate in 1.0 mM concentration and ascorbic acid, glutathione in 0.1 mM

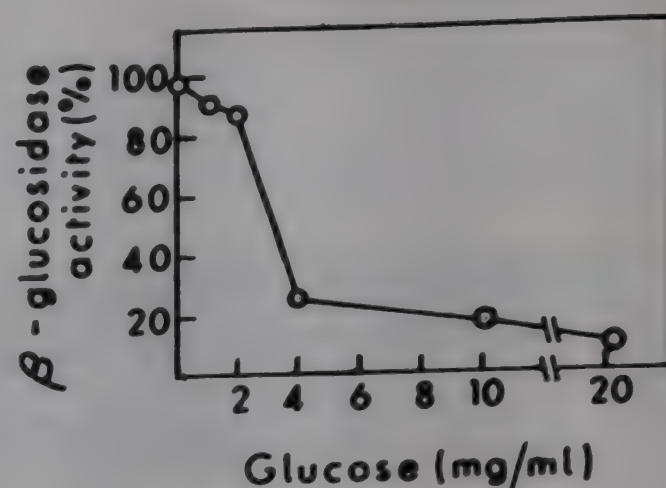


Fig. 1—Inhibition of β -glucosidase activity by glucose

Table 1—Effect of some organic substances on activity of cellulases and β -glucosidase

Organic substance	Activity (IU/ml)		
	CMCase	FPA	β -glucosidase
Control	3.61	0.46	12.59
EDTA	3.61	0.33	9.62
SDS	3.61	0.37	13.33
L-cysteine	5.10	0.61	14.80
Ammonium thiocyanate	3.33	0.46	12.96
Ascorbic acid	3.61	0.54	12.68
Glutathione	3.55	0.46	12.20

concentration were separately added to the enzyme reaction mixture of standard assay system. Among the different organic compounds tested (Table 1). L-cysteine increased the activity of CMCase, FPA and β -glucosidase.

Saccharification of cellulosic wastes — Hydrolysis of untreated and alkali treated rice straw, bagasse, jute stick in 2 and 5 per cent concentration were carried out using different volume of enzyme at pH 4.8 and temperature 60°C. The reducing sugar produced was estimated from 24 h to 96 h using dinitro-salicylic acid method¹¹. Results are shown in Figs 2 & 3 and Table 2. Maximum saccharification (58.95%) was obtained with 2 per cent alkali-treated rice straw at 72 h of incubation at 60°C.

Discussion

The cellulase enzyme system of *Aspergillus oryzae* culture filtrate was found to be rich in β -glucosidase (12.59 IU/ml). This is of importance because low level of β -glucosidase in a cellulase system results in the accumulation of cellobiose which decreases the rate and extent of cellulose hydrolysis. Glucose has some inhibitory effect on β -glucosidase activity (Fig.1).

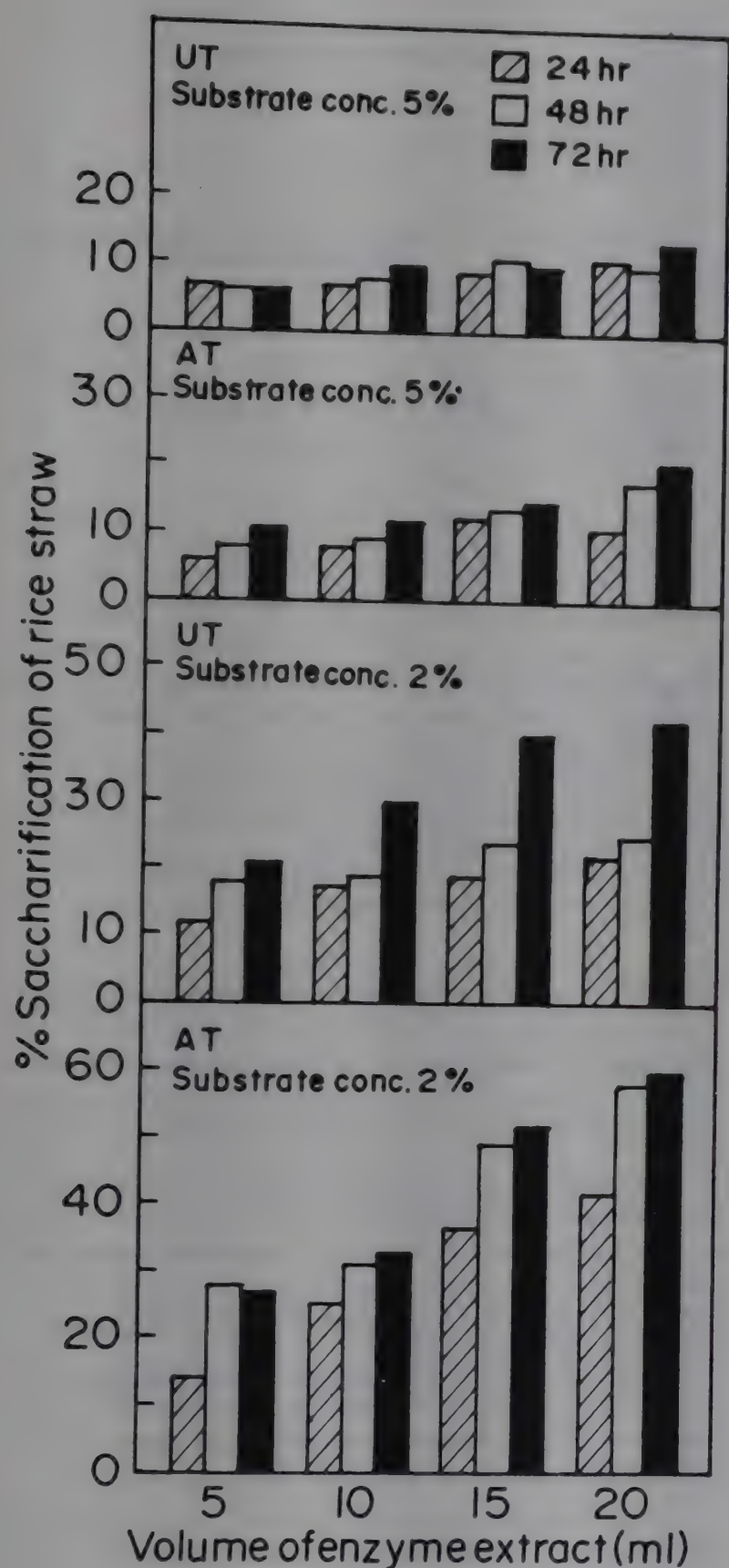


Fig. 2—Effect of enzyme and substrate concentration on the saccharification of rice straw (AT - alkali treated, UT - untreated)

The per cent saccharification increased with increasing concentration of culture filtrate. An increase in time of reaction up to 72 h resulted in increased sugar production. Further increase in time of incubation did not show any significant increase in saccharification. This could possibly be due to either enzyme inactivation, hydrolysis of the readily susceptible amorphous regions leaving the more

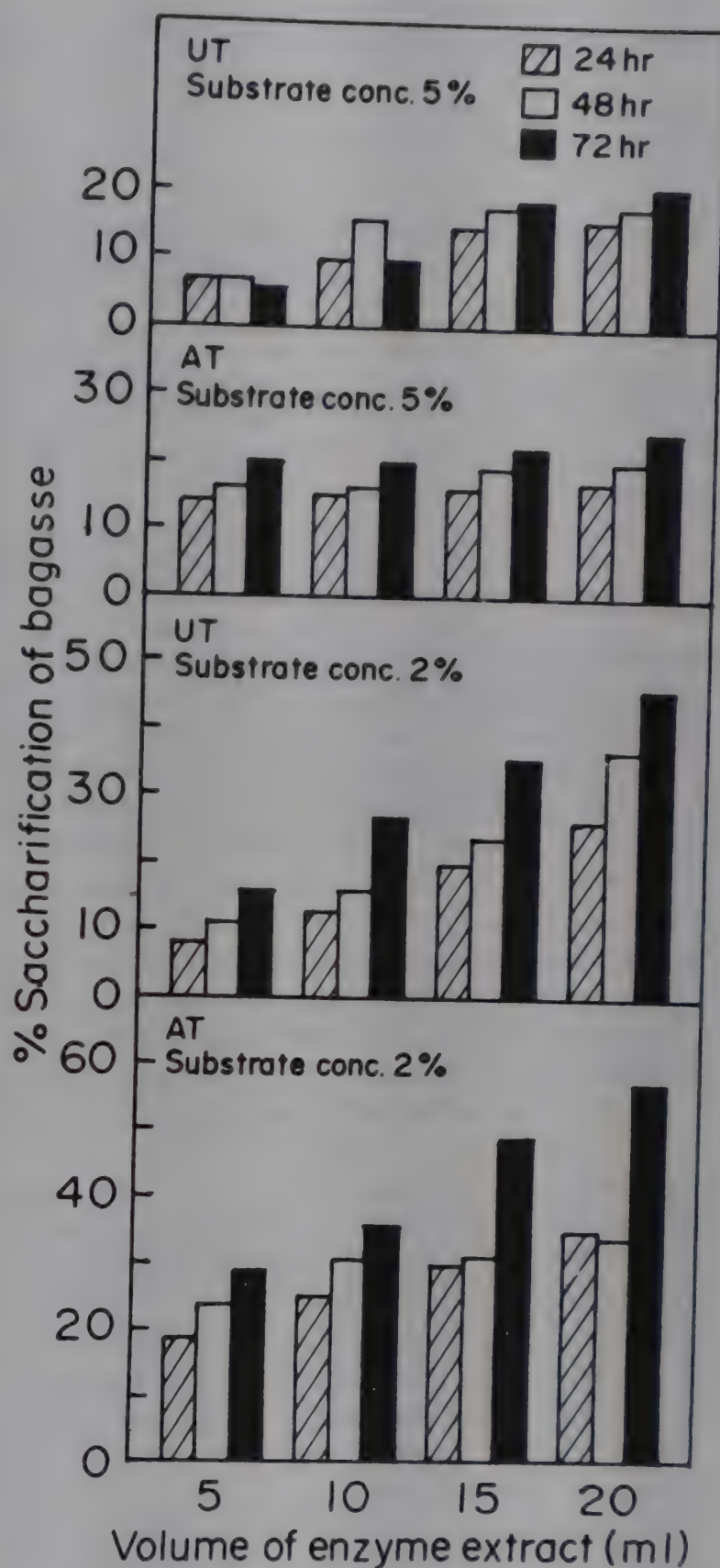


Fig. 3—Effect of enzyme and substrate concentration on saccharification of bagasse (AT - alkali treated, UT - untreated)

resistant substrate or the general accumulation of glucose leading to catabolite repression¹⁶.

Greater amount of saccharification was obtained with alkali-treated rice-straw and bagasse as compared to untreated substrates. It is clear that saccharification was lowest when lignin was present in the untreated substrate indicating the lignin, which does not chemically inhibit cellulase, may act as a

Table 2—Effect of concentration of the enzyme from *A. oryzae* and substrate concentration on hydrolysis of untreated (UT) and alkali treated (AT) jute stick

Substrate	Enzyme extract volume ml	Substrate concentration (%)					
		2.0			5.0		
		% saccharification at			% saccharification at		
		24 h	48 h	72 h	24 h	48 h	72 h
Jute stick (AT)	10	7.11	8.91	9.90	9.36	12.06	11.61
	15	11.46	15.14	19.35	12.91	16.96	21.92
	20	14.77	20.07	26.10	17.37	22.32	29.97
Jute stick (UT)	10	5.76	8.91	10.71	11.40	15.14	16.9
	15	12.24	15.41	16.06	14.80	19.35	24.1
	20	17.37	21.42	24.12	21.70	24.0	30.6

barrier in reducing the accessibility of hemicellulose or cellulose to the respective enzymes^{17,18}. It was also observed that saccharification decreased with increasing substrate concentration in case of rice straw and bagasse. Similar results were obtained with delignified bagasse and rice straw using *Trichoderma resei*, *Sclerotium rolofsii* and *Pellicularia filamentosa* of reducing sugar and per cent saccharification of

There is no significant difference in the production of reducing sugar and percent saccharification of alkali treated (AT) and untreated (UT) jute stick using the culture filtrate (Table 2). This is probably due to the tough nature of the substrate.

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Enzymatic hydrolysis of starch to glucose, and immobilization of amyloglucosidase in calcium alginate gel

Lalitagauri Ray and S K Majumdar

Department of Food Technology & Biochemical Engineering, Jadavpur University, Calcutta-700 032

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Aspergillus oryzae amylases (α -amylase and amyloglucosidase) were used for both liquefaction and saccharification of starch from different sources. For liquefaction of starch (25 ml starch-enzyme mixture in 50 ml Erlenmeyer flask), the optimum conditions were pH 5.1, temperature 40°C, incubation period 2 hr with shaking at 90 r.p.m. and for saccharification, the optimum parameters are as follows pH 4.8, temperature 50°C, incubation time 22 hr. The maximum conversion of potato, tapioca, shati and soluble starch to glucose were 82, 82, 70 and 96.9 per cent respectively. Then amyloglucosidase from *A. oryzae* was partially purified and immobilized in calcium alginate gel matrix that retained 77 per cent of the activity of free enzyme. Optimum pH of the enzyme was shifted from 4.8 to 5.1 by immobilization optimum temperature remaining the same. Km values for free and immobilized enzyme were 0.4 and 0.1 per cent respectively. Immobilized enzyme can be stored at 4°C for 28 days without any significant loss of activities.

Starch is the second most abundant renewable biopolymer present on earth and accounts more than 10^9 tonnes annually¹. The conventional process still employed to manufacture glucose from starch by almost all manufacturers in India is the acid hydrolysis. The enzymatic process improves both process efficiency and product quality. It overcomes the limitations of acid process in regard to production of colouring, flavouring substance and other impurities, which are the main objections for the usage of glucose syrups or crystals in the food or pharmaceutical industries. The enzymatic process requires a low temperature instead of 140°-160°C as in the case of acid hydrolysis. Furthermore the process of acid hydrolysis has a restriction regarding the concentration of feed (maximum 12% starch) slurry, whereas in case of enzymatic process² the feed concentration can be upto 35%. Amyloglucosidase can attack both alpha 1-4 and alpha 1-6 glucosidic linkages of starch molecule to produce glucose. The glucose produced can be used for the production of high fructose syrup and various other food products^{3,4}. The use of immobilized enzyme system for starch hydrolysis allows reuse of the enzyme and separation of products from biocatalysts among the advantages⁵.

The present study describes (i) the use of crude enzyme extract containing α -amylase and amyloglucosidase for liquefaction and saccharification of starch from different sources and (ii)

successful immobilization of the partially purified amyloglucosidase in calcium alginate gel in presence of glutaraldehyde.

Methods and Materials

Microorganism—Amylase producing mold *Aspergillus oryzae* was grown in Czapek Dox agar medium for 5 days at $28 \pm 2^\circ\text{C}$ and the culture was stored in a refrigerator at 0-4°C.

Production of Crude Enzyme Extract—25 g sterilised wheat bran containing 50 per cent moisture taken in a 500 ml Erlenmeyer flask was mixed thoroughly with 5 ml spore suspension (7.75×10^8 spores) of *A. oryzae* and incubated at $28 \pm 2^\circ\text{C}$ for 7 days under stationary condition for maximum enzyme production. The mold bran was then soaked with 100 ml distilled water and kept in the refrigerator overnight and then squeezed through cheese cloth. The extract was centrifugated at 10,000 r.p.m. at 5°C for 10 min. The clear centrifugate was used as crude enzyme extract.

Estimation of Enzyme Activity

Alpha-amylase— α -amylase activity (amount of enzyme which hydrolyzes 10 mg starch/min) was determined using the method of Manning and Campbell⁶.

Amyloglucosidase—The amyloglucosidase activity (amount of enzyme required to release 1 μ mole of glucose/ml/min) was determined by

incubating 1.5 ml of 4 per cent soluble starch solution in 0.2 M acetate buffer (pH 4.8) and 0.5 ml suitably diluted enzyme preparation at 50°C for 1 hr and estimating the glucose produced using Tauber's method⁷.

Enzymatic Conversion of Starch to Glucose—For enzymatic conversion of starch to glucose, starch (7.5 g) from each source viz., potato, tapioca, shati and soluble starch was stirred with 0.2 M acetate buffer (pH 5.1) to form a slurry. The slurry was first gelatinized by heating at 65–70°C for 15–20 min on a hot water bath. Different volumes of crude enzyme extract were added to the gelatinized starch slurry to have the total volume at 25 ml. The starch enzyme slurry (pH 5.1) was incubated at 40°C for 2 hr with shaking for liquefaction then after adjustment of pH at 4.8 the liquefied starch was incubated for 22 hr at 50°C for saccharification. Enzymatic conversion process was also studied with larger volume of slurry containing 45 g starch and 90 ml crude enzyme extract was taken in a 500 ml Erlenmeyer flask and treated as described before.

Estimation of the Extent of Starch Hydrolysis—The extent of starch hydrolysis during liquefaction and saccharification processes were checked by estimating the glucose produced using Tauber's method⁷.

Partial Purification of Amyloglucosidase—The crude enzyme (90 ml) preparation was concentrated five fold using a flash evaporator. The pH of the concentrate was adjusted to 4.8. The enzyme was precipitated using 50 per cent acetone in presence of 0.2 per cent sodium chloride. The precipitated enzyme was washed with 50 per cent acetone and dissolved in 18 ml 0.2 M acetate buffer, pH 5.1.

Immobilization of Enzyme—For immobilization of enzyme 2.9 ml of different concentrations of sodium alginate was mixed with 0.1 ml partially purified enzyme solution and adding dropwise (using a hypodermic syringe, 10 ml) in 4 per cent calcium chloride solution containing 1.0 per cent glutaraldehyde. The gel beads thus formed were left for 15 min. at 4°C and then washed thoroughly with buffer, air dried and used as immobilized enzyme.

Assay of Immobilized Enzyme—In case of immobilized enzyme, the immobilized beads (diameter 2–4 mm) prepared from equivalent amount of enzyme were used for immobilized enzyme assay using the same procedure as that of free enzyme.

Results and Discussion

Estimation of α -Amylase and Amyloglucosidase Activity in the Crude Enzyme Preparation—The

activities of α amylase and amyloglucosidase were determined by usual procedure. The activities of α amylase and amyloglucosidase are 11 and 27.2 u/ml. Optimum temperature and pH for the maximum activities of α -amylase and amyloglucosidase were 40°C & 50°C, and 5.1 & 4.8 respectively.

Enzymatic Hydrolysis of Starch—30 per cent starch (i.e. 7.5 g/25 ml reaction mixture) from four different sources e.g. potato, shati, tapioca and soluble starch were used for this purpose.

Time of Liquefaction—Liquefaction was carried out as described before using different volume of enzyme by varying the time from 30 min to 6 hr with shaking and it was found that liquefaction was completed in 2 hr.

Time of Saccharification—Saccharification of the liquefied starch was carried out with different volumes of enzyme (5, 10, 15, 20 ml) as described before. The extent of saccharification was determined by estimation of reducing sugar at definite time intervals and it was found that saccharification was completed at 22 hr of incubation. The optimum volume of enzyme for maximum saccharification was 15 ml i.e. optimum level of α amylase and amyloglucosidase were 165 u α -amylase i.e., 22 u/g of starch and 408 u amyloglucosidase i.e. 54.4 u/g of starch. The maximum conversion obtained with potato, shati, tapioca and soluble starch were 82, 70, 82, 96.9 per cent. The maximum sugar was produced using soluble starch (Table 1).

Enzymatic conversion process was also carried out with larger volume of slurry containing soluble starch and potato starch. 150 ml starch-enzyme slurry containing 45 g starch and 90 ml crude enzyme extract was taken in a 500 ml Erlenmeyer flask and treated as described before. Results are shown in Fig. 1. The percentage of conversion of soluble starch and potato starch were found to be 88.5 and 77.2 per cent.

Preparation of Immobilized Enzyme System

(i) **Effect of Alginate**—Immobilized enzyme beads were prepared, other conditions remaining the same, (method described as before) using different concentrations of alginate (1.0 to 4.0 per cent) and maximum activity was retained by the immobilized beads prepared with 3.0 per cent alginate concentration.

(ii) **Effect of Calcium Chloride**—Different concentrations of calcium chloride (1.0 to 4.0 per cent) were used (other conditions remaining the same) for immobilization of amyloglucosidase and 2.0 per cent salt solution was found to be optimum.

(iii) **Effect of Glutaraldehyde**—Glutaraldehyde concentration was varied from 0.2 per cent to 2.0 per

Table 1—Effect of enzyme concentration on hydrolysis of starch from different sources

Volume of enzyme extract (ml)	Level of enzyme				Glucose produced from different source of starch				per cent conversion of starch to glucose			
	α -amylase		Amyloglucosidase		Soluble starch	Potato	Tapioca	Shoti	Soluble starch	Potato	Tapioca	Shoti
	Total unit	u/g of starch	Total unit	u/g of starch								
10	110	14.66	272	36.31	6.82	5.31	4.959	4.99	82.7	64.4	60.0	60.6
15	165	22.00	408	54.4	8.0	6.76	6.75	5.77	96.9	82.0	82.0	70.0
20	220	29.33	544	72.53	7.92	6.74	6.775	5.7	96.0	82.0	82.0	70.0

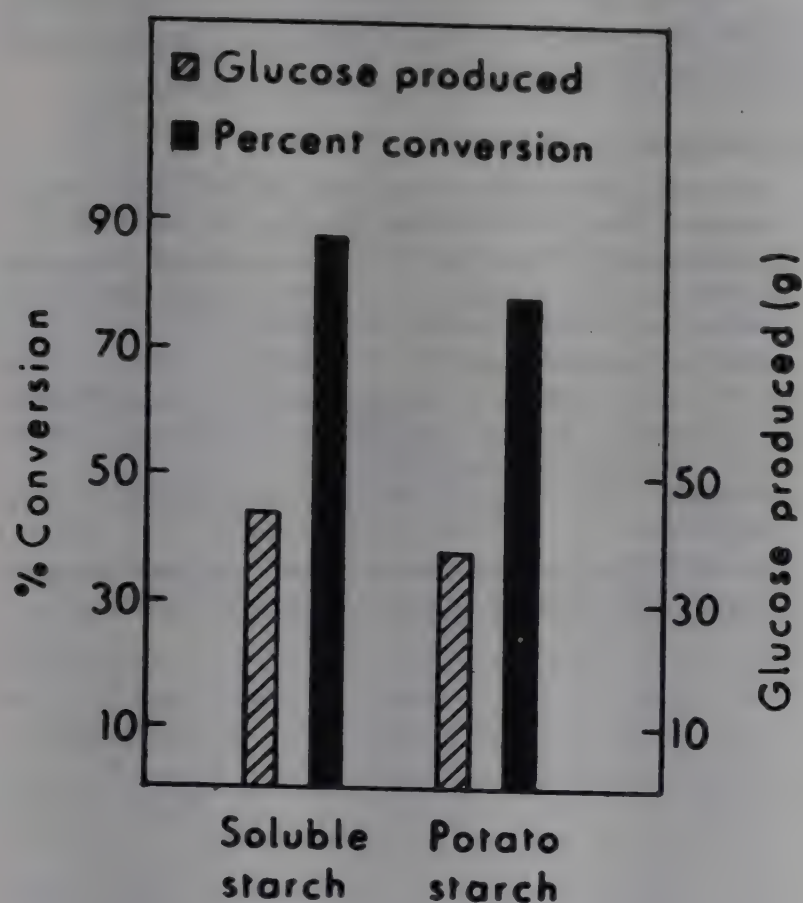


Fig. 1—Production of glucose from soluble starch and potato starch

cent other conditions remaining the same and 1.0 per cent of glutaraldehyde was found to be most suitable for immobilization of the enzyme.

(iv) Determination of Optimum Time of Immobilization—The time for preparing immobilized beads were varied from 5 min to 2 hr and 15 min was selected as optimum.

(v) Determination of the Optimum Temperature and pH for the Maximum Activity of Immobilized Enzyme—Assay of immobilized enzyme (described before) was performed using different incubation temperature (from 40°C to 70°C) and also at different pH of the reaction mixture (4.4 to 5.5) other conditions remaining the same in each case. The optimum temperature for the activity of immobilized

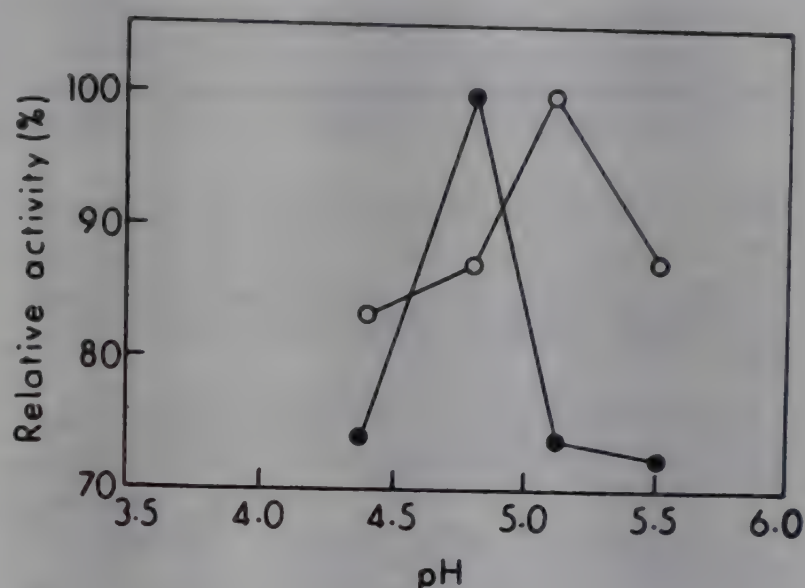


Fig. 2—Optimum temperature for free (○—○) and immobilized (●—●) amyloglucosidase activity

amyloglucosidase was 50°C i.e. same as that of free enzyme (Fig. 2) but the optimum pH for the immobilized enzyme was shifted from 4.8 to 5.1 (Fig. 3).

Effect of Size of Immobilized Beads—Effect of size of immobilized beads were also studied using hypodermic syringes of different diameters and it was observed that beads of 2.5 to 3.0 mm showed higher enzyme activity. It was also observed that 3 per cent calcium alginate entrapped enzyme retained 77 per cent of activity of free enzyme i.e. 27.2 u/ml.

pH Stability of the Free (Partially Purified) and Immobilized Enzyme—The pH stability of free and immobilized enzyme was determined by incubating them with 5.0 ml 0.2 M acetate buffer at different pHs (4.0 to 6.0) at 30°C for 20 hr and then the stability of amyloglucosidase was determined using the standard assay procedure. The free (partially purified) and immobilized enzymes were most stable at pH 4.8 and 5.1 respectively.

Thermostability of Free (Partially Purified) and Immobilized Amyloglucosidase—The thermostability of free and immobilized enzymes was determined by incubating the beads in 0.2 M acetate

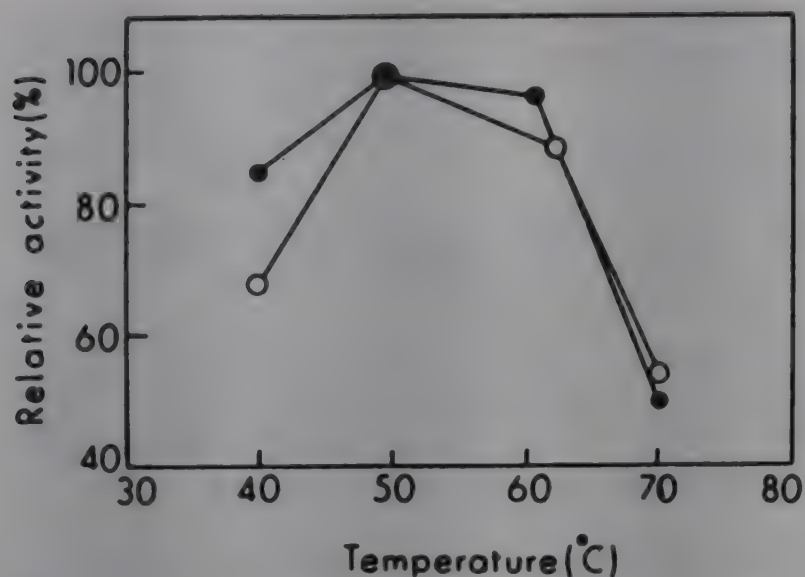


Fig. 3—Effect of pH on amyloglucosidase activity in free (○—○) and immobilized (○—○) state

buffer at optimum pH using different incubation temperatures (from -4°C to 30°C) for 20 hr. The residual activities were determined. Free and immobilized enzymes both were most stable at 4.0°C .

Reaction Kinetics—To determine the K_m values of free and immobilized enzymes, the reaction (assay) was carried out with different substrate concentrations at 50°C and pH 4.8 and 5.1 respectively for 1 hr keeping the enzyme

concentration constant. The K_m values of free and immobilized enzymes were 0.4 and 0.1 per cent respectively.

Storage Stability—Storage stability of the alginate-entrapped enzyme beads were studied using 0.2 M acetate buffer (pH 5.1) under refrigeration (4°C) and the activity was measured at different time. The immobilized enzymes were stable and could be stored in the refrigerator for 28 days without any significant loss of enzyme activity.

Acknowledgement

Authors gratefully acknowledge the financial help of the Department of Biotechnology, Government of India in carrying out this research work.

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Effect of adsorbability of iron contents by aluminium oxide in the commercial crude sodium sulphide

M P S Chandrawat, Jyotsna Agarwal & Gopal Krishan Khatri
Department of Chemistry, RR (P Gr/Auto) College, Alwar (Raj.)

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The paper reports the investigations on adsorbability of ferri/ferrous impurities found in commercial grade sodium sulphide. The later product is unsuitable for manufacture of pharmaceutical grade chemicals and dyes chemicals. The authors have carried out experiments on the use of aluminium oxide as an adsorbent in different proportions in the aqueous solution of commercial grade sodium sulphide. The findings are quite encouraging.

Sodium sulphide is widely used in tanneris, dyestuff, textile industries etc¹⁻⁵. Applications of sodium sulphide are greatly affected by contamination of iron contents in traces in it. Even in traces, iron contents reduce market cost of Na₂S to the extent of 50 per cent. Its utility in the manufacture of dyes is also affected adversely in presence of iron impurities. Thus to improve the quality of Na₂S authors have tried amorphous aluminium oxide as adsorbant. The authors have used it because of its large specific surface area in the finely powdered state. This property plays an important part in the adsorption process^{1,2,5-7}.

Materials

Materials used for study were procured from the following respective sources.

Sodium sulphide (Crude commercial product)—Supernatant solution obtained after soda ash treatment of barium sulphide extract contains sodium sulphide as the main by-product. This supernatant solution on evaporation gives flakes of crude commercial sodium sulphide, which is usually contaminated with iron contents as an impurity. The crude sodium sulphide was prepared by the authors in the lab. by carbothermal reduction of barytes.

Chemical reagents (Pot. thiocynate, KMnO₄, HCl-4N etc.)—Most of the chemical reagents of AR grade (BDH products) were procured from the Deptt. of chemistry, RR (P Gr/Auto) College, Alwar.

Experimental Procedure

Experiments were conducted to investigate the adsorbability of alumina for iron contents present in commercial crude sodium sulphide as follows.

Preparation of reagents—(a) Pot. thiocyanate solution 20 g. of AR potassium thiocyanate is dissolved in 100 ml of distilled water.

(b) KMnO₄ solution - 2 g. of KMnO₄ AR is dissolved in 50 ml of distilled water and volume is made upto one litre.

(c) HCl (4N) - 36 ml of pure conc. HCl is added into 50 ml of distilled water and volume is made up to 100 ml.

Preparation of sample solutions—5 g of Na₂S (iron contaminated) is dissolved in 100 ml of distilled water. In each solution the different amounts of finely powdered aluminium oxide (1, 5, 10, 15 and 20 per cent by wt. of Na₂S) was added. The solutions were warmed slightly on the low heat with vigorous shaking for 15 minute and filtered. In the filterates 25 ml of conc. AR HCl was added. To expel the excess of acid the solutions were evaporated nearly to dryness. The obtained residues were diluted with water. To oxidise the iron to the Fe³⁺ state, a dilute solution of potassium permagnate was added in the above solution till the slight pink colour appeared. The volume of the solutions were made upto 250 ml with distilled water. From these solutions, estimation of iron was done as per the standard procedures^{8,12}.

Method—To find out the percentage of iron contents in treated sodium sulphide, known amount of 50 ml sample solution is placed in a nessler cylinder. In this solution 5 ml of pot. thiocynate solution and 2-4 ml of 4N-HCl is added.

In another nessler tube 50 ml of distilled water, all the above reagents are added and the standard iron solution is run from burette till the colours are matched.

Calculations were made according to the available Indian Standards⁸⁻¹². Observed results are summarised in the Table 1 (1 ml of standard iron soln. of the sample contains 0.1 mg of iron)¹².

Discussion

Adsorbability of iron contents by aluminium oxide powder is revealed in the Table 1. It is noted from the Table 1 that incorporation of aluminium oxide reduces iron contents considerably. Even slight addition (as small as 1%) is sufficient to reduce contamination of iron contents from 1.5 mg to 0.1 mg. This amounts to a very smooth and convenient reduction of iron contents to the extent of 0.005 per cent or even less in the contaminated commercial Na₂S. The plausible reason for this may be the formation of oppositely charged colloidal systems by iron and alumina in the solution. After stirring these solutions a gelatinous coprecipitate is coagulated which is filterable easily and therefore can be removed by filtration. It is important to note that according to the above proposed mechanism, elimination of iron contents should be improved further by increasing surface area of amorphous alumina and efficiency of filtration.

Conclusion

Aluminium oxide (amorphous) is a good adsorbent even in very minute amounts. After adding an optimum amount of aluminium oxide, further additions do not bring any remarkable change in iron contents.

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Table 1—Effect of adsorbability of iron contents by aluminium oxide in the flakes of sodium sulphide

S. No.	Na ₂ S used in grams	Aluminium oxide used in grams	Observed value (ml.)	Iron present in sodium sulphide after adsorption as 1 ml = 0.1 mg Fe
1	5.0	0.00	15.0	1.5
2	5.0	0.05	1.2	0.12
3	5.0	0.25	1.0	0.10
4	5.0	0.50	1.0	0.1
5	5.0	0.75	1.0	0.1
6	5.0	1.00	1.0	0.1

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Removal of organic matters from sugar mill effluent using bagasse fly ash activated carbon

I D Mall, N Mishra* & I M Mishra

Department of Chemical Engineering, University of Roorkee, Roorkee

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The possibility of utilising bagasse fly ash and activated carbon for the removal of COD and colour from sugar mill effluent has been evaluated in this investigation. Physico-chemical characteristics of bagasse fly ash and activated carbon and their efficiency in removing organics have been presented. Percent removal was found to be maximum at pH 5. Removal also increases with decreasing initial concentration. First order removal kinetics was observed for both bagasse fly ash and activated carbon. As the removal efficiency of bagasse fly ash and activated carbon were found to be comparable, bagasse fly ash would have good potential as a substitute for activated carbon for adsorptive removal of organics from sugar mill effluent.

Sugar industry is the second largest agro-based industries in India which is one of the largest producers of sugar in the world^{1,2}. At present 377 sugar mills are in operation with about 100 new mills in the pipeline, the production of sugar production has crossed 12 million tonnes in the year 1991-1992. By 2000 A.D. sugar production is expected to be 16 million tonnes². Sugar mills in India employ about 2,00,000 persons and about 35 million farmers (including their families) constituting about 7 per cent of the rural population are engaged in sugar cane farming³. Majority of sugar mills are located in the rural area in the States of UP, Bihar, Andhra Pradesh and Maharashtra.

Sugar industry has, however, been one of the major polluting industries. Sugar mills generate large volume of waste water with the characteristics of high BOD, COD, suspended matter and dissolved solids, oil and grease, etc.³. Normal mills generate about 40 kl of waste water per 100 tonnes of sugar produced⁴. This volume can be reduced drastically following recycling techniques. The typical characteristics of sugar mill effluent are given in Table 1.

Various sources of waste water generation in sugar mills are mill house, cooling water, boiler blow down, rotary filter house and other miscellaneous sources. The methods used by sugar mills for treatment of effluent are lagooning, aeration, activated sludge treatment, and bio-filtration.

There is growing concern over the pollution problem from the sugar mills because of their non-compliance of the MINAS⁵ laid down by the Central Board for Prevention and Control of Water Pollution Board (Table 2).

Table 1—Characteristics of effluent from a typical Indian sugar mill

Characteristics	Range of value
BOD, mg/l	1000-1500
COD, mg/l	2000-3000
pH	4.5-7.0
Temperature, °C	25-35
Total solids, mg/l	2000-2500
Total suspended solids, mg/l	300-600
Oil and grease, mg/l	5-30

Table 2—Minimum National Standards (MINAS) for sugar industries

Parameters	Disposal on land	Disposal into water bodies/ sewers
BOD, mg/l	100	30
Suspended solid, mg/l	100	30
Oil and grease, mg/l	—	10

Molasses and bagasse are the two major byproducts of sugar industry. About 0.33 tonne of bagasse is produced per tonne of cane crushed and about 90-95 per cent of bagasse is consumed as fuel and large amount of fly ash is generated from these boilers.

Amongst treatment processes, adsorption using activated carbon promises a potential method for tertiary stage treatment of the industrial effluents for the removal of colour, heavy metals and refractory organic compounds. However, high cost of activated carbon and 10-15 per cent loss in regeneration have been deterrents in the utilisation of activated carbon in the

*Institute of Engineering and Technology, Lucknow

developing countries. As substitute to activated carbon, fly ash, peat, wood, lignite, and agricultural residues have been tried⁶⁻¹¹.

In an earlier investigation it was reported that bagasse fly ash can be used as an efficient adsorbent for the removal of COD from sugar mill effluent¹². The present investigation provides an comparison of the characteristics and efficiency of bagasse fly ash and activated carbon in the removal of organics from sugar mill effluent. Various parameters investigated include effect of contact time, initial COD concentration, adsorbent dose. Adsorption isotherms and kinetics of COD removal have also been presented.

Availability of Bagasse Fly Ash

Amount of bagasse fly ash generated from the bagasse-fired boilers varies widely from boiler to boiler depending upon the efficiency of the boilers, ranging from 50 to 70 per cent on gross heating value of bagasse in the case of new boilers¹³. With an overall collection efficiency of 80 per cent, it is estimated that fly ash availability from sugar industries would be of the order of 0.64 million tonnes^{13,14}. The value of uncontrolled emission of suspended particulate matter from various types of boilers are given in Table 3^{13,14}. The combustible matter in bagasse fly ash ranges from 35-70 per cent^{12,14}.

Experimental Procedure

For evaluation of suitability of the bagasse fly ash and its comparison with activated carbon, the experimental programmes consisted of: (i) characteristics of fly ash and activated carbon, and (ii) batch studies on adsorption for evaluation of effect of operating parameters.

Bagasse fly ash and activated carbon were characterised for bulk density, fixed carbon, volatile matter, ash, chemical analysis and particle size analysis. For morphology, X-ray diffraction and scanning electron microscope (SEM) were used. COD, BOD, pH and total dissolved solid of the jaggery solution and sugar mill effluent were determined as per standard methods. For adsorption kinetics, evaluation of effect of various parameters on the adsorption and adsorption isotherms, batch experiments were conducted by contacting 100 cc of synthetic waste water prepared from jaggery and 1.5 g of bagasse fly ash and activated carbon. The COD of supernatant treated waste water was determined as per standard method. COD removal studies were also conducted by contacting the bagasse fly ash and activated carbon with sugar mill effluent. As maximum removal of COD was observed at pH = 5.0 for jaggery solution using bagasse fly ash in earlier investigation¹², the pH in the

Table 3—Uncontrolled suspended particulate matter emission from various types of boilers

Types of boiler	Quantity of emission mg/nm ³
Natural draft boiler	180-250
Induced draft boiler	250-1500
Sprader stoker type boiler	2000-4500
Balanced draft boiler	2000-5000

Table 4—Characteristics of bagasse fly ash and activated carbon

Parameters	Bagasse	Activated carbon
Proximate analyses		
Bulk density, kg/m ³	244.00	600.90
Moisture	8.11	9.26
Ash	30.74	11.10
Volatile matter	22.46	2.55
Combustible matter	69.26	86.35
Surface area, m ² /g	410.00	488.00
Chemical analyses		
Silica, %	12.37	
Alumina, %	6.84	
Calcium, %	0.03	
M-alkalinity, %	0.80	
P-alkalinity, %	0.10	

Particle size analyses of bagasse and activated carbon

Bagasse fly ash			Activated carbon		
Size, micron	Weight, %		Size, mm	Weight, %	
> 850	8.20		> 4.760	1.5	
< 850	> 710	12.50	< 4.760	> 4.000	8.0
< 710	> 600	0.65	< 4.000	> 2.818	13.0
< 600	> 500	0.85	< 2.818	> 2.099	35.0
< 500	> 355	12.90	< 2.099	> 1.400	37.0
< 355	> 300	14.90	< 1.400	> 1.205	2.5
< 300	> 180	29.30	< 1.205	> 1.201	1.5
< 180	> 125	3.20	< 1.201	> 1.00	1.1
< 125	> 075	8.40	< 1.00		0.4
< 075	> 045	1.65			
< 045					

present investigation was maintained 5.0 throughout the experiments.

Results and Discussion

Characteristics of bagasse fly ash and activated carbon—Bagasse fly ash and activated carbon characteristics are presented in the Table 4. Bagasse fly ash

consists of mainly unburnt carbon and bagasse. The ash is very light as compared to activated carbon. The bulk density of fly ash vary depending upon the amount of unburnt carbon. Combustible matter in the bagasse fly ash and activated carbon was found to be 86.35 and 69.26 per cent respectively. Chemical analysis shows that carbon, silica and alumina are major constituents in bagasse fly ash. However, silica and alumina contents are very low in bagasse fly ash as compared to coal fly ash. The particle size analysis of bagasse fly ash and activated carbon are given in Table 4.

The X-ray diffractogram of bagasse fly ash and activated carbon are shown in Fig. 1. The major components identified in bagasse fly ash are quartz multiple, sillimanite whereas quartz crystoballite and mulite are the major constituents of activated carbon^{15,16}. No diffraction peaks corresponding to crystalline carbon was observed in both fly ash and activated carbon. The broad peaks in both the samples may be due to amorphous form of the silica. The scanning electron micrographs of fly ash and activated carbon show different morphology. Presence of some biomass in bagasse fly ash is also seen in the SEM of bagasse fly ash.

Characterisation of synthetic waste water and sugar mill effluent—Synthetic waste water prepared by dissolving jaggery in water and sugar mill effluent was characterised for COD, BOD, pH and total dissolved solids and the results are given in Table 5.

Effect of adsorbent dose—The effect of adsorbent dose on removal by bagasse fly ash is shown in Fig. 2. From the figure it can be seen that the per cent removal of COD increases with increase in the adsorbent dose while removal per unit weight of adsorbent increases with the decrease in adsorbent dose.

Effect of initial concentration and contact time—The effect of initial concentration on removal of COD by bagasse fly ash and activated carbon is shown in Figs 3 and 4. Removal of COD per unit weight of ash and activated carbon was found to increase with increase in initial COD concentration. However, per cent removal increase with decrease in initial COD concentration. The equilibrium time was 12 h in case of bagasse fly ash and 16 h for activated carbon. For initial concentration of 476.0 mg/l per cent removal and removal mg/g of adsorbent was 61.8 per cent and 19.6 for bagasse fly ash and 58.8 per cent and 18.67 for activated carbon. The effect of initial concentration on removal of colour by fly ash and activated carbon was also examined and it was observed that at COD concentration of 550 mg/l, the removal of colour was almost 100 per cent.

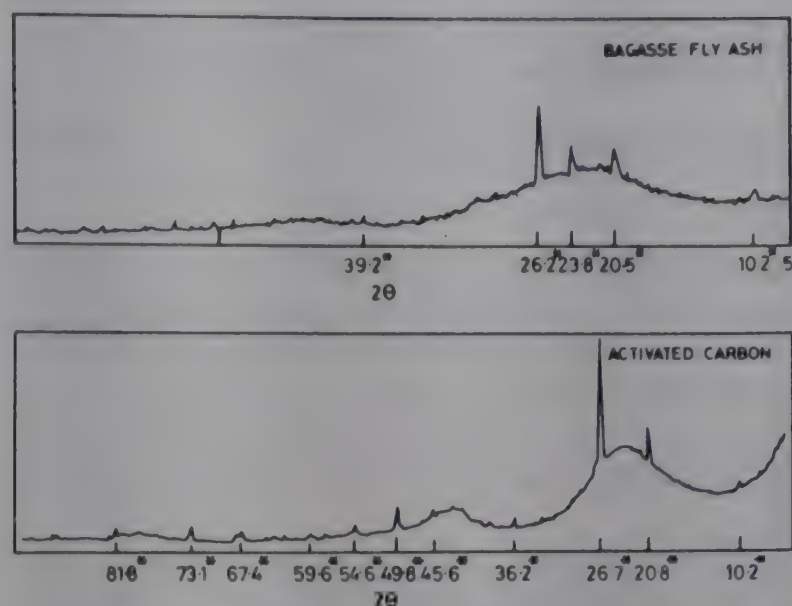


Fig. 1—X-ray diffractogram of bagasse fly ash and activated carbon

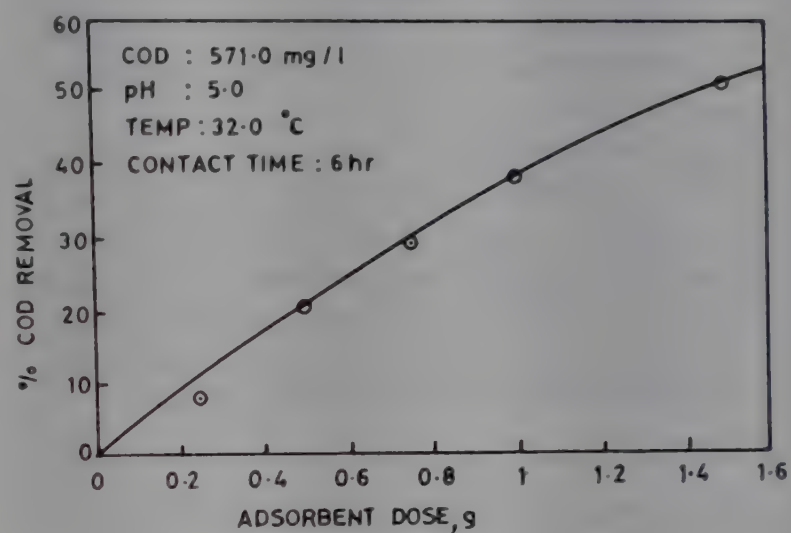


Fig. 2—Effect of adsorbent dose on removal of COD by bagasse fly ash

Table 5—Characteristics of waste water

Characteristics	Sugar mill effluent	Jaggery solution, 1 g/l
COD, mg/l	528	812
BOD, mg/l	210	395
pH	6.69	4.98
Total dissolved Solids, mg/l	4.85	236

COD removal kinetics—The kinetics data are of significant importance for evaluation of design performance of adsorber. The kinetics of solute transport from solution phase to the surface of adsorbent particle is either by film or external diffusion, pore diffusion, pore surface diffusion and adsorption on the pore surface or the combined effect of more than one of these^{17,18}. The kinetics of the removal of COD by bagasse fly ash and activated carbon have been presented using the following approaches: (i) Adsorption rate constant using Lagergren first order expression, and (ii) Intraparticle diffusion.

The removal of COD by bagasse fly ash and activated carbon obeys the following first order rate expression proposed by Lagergren¹⁹.

$$\log (q_e - q) = \log q_e - (k/2.303) t$$

where q and q_e is the amount of COD removed per unit weight of adsorbent at time t and equilibrium, k is adsorption rate constant. The value of rate constant k determined from linear plot of $\log (q_e - q)$ versus t (Fig. 5) is 0.187 and 0.1567 h^{-1} for fly ash and activated carbon respectively at initial concentration of 467 mg/l.

In diffusion studies rate processes are usually expressed in terms of square root of time²⁰. The plot of amount of COD removed versus $t^{0.5}$ is given in Fig. 6 for both bagasse fly ash and activated carbon. It may be seen that there are two separate regions—the initial pore diffusion due to external mass transfer effects followed by the intraparticle diffusion²¹.

Adsorption isotherms—Adsorption equilibrium data are conveniently represented by adsorption isotherms which are helpful in determining the adsorption capacities of different adsorbents. Freundlich and Langmuir isotherms were used to analyse the equilibrium data for removal of COD from jaggery solution by bagasse fly ash and activated carbon.

Freundlich Isotherm: $q_e = a_F C_e^{1/n}$

Langmuir Isotherm: $1/q_e = 1/Q_0 + (1/Q_0 b) 1/C_e$

where C_e and q_e are the concentration and the amount adsorbed at equilibrium, a_F and n are the Freundlich constants, Q_0 and b are the Langmuir isotherm constants.

Both the Freundlich and Langmuir isotherms were found applicable (Figs 7-9). The values of Freundlich and Langmuir isotherms are given in Table 6.

Removal of COD and colour from sugar mill effluent using bagasse fly ash and activated carbon—The suitability of bagasse fly ash for removal of COD from sugar mill effluent was also studied and results were compared with activated carbon. Higher removal was observed in case of bagasse fly ash. About 54.73 per cent and 41.76 per cent COD was possible with bagasse fly ash and activated carbon respectively for an adsorbent dose of 15 kg/m^3 and initial concentration of 528 mg/l. 100 per cent colour removal was observed at this initial concentration and adsorbent dose in case of both bagasse fly ash and activated carbon.

Utilisation of bagasse fly ash after treatment

The heating value of bagasse fly ash which contains about 30-60 per cent unburnt carbon and bagasse has

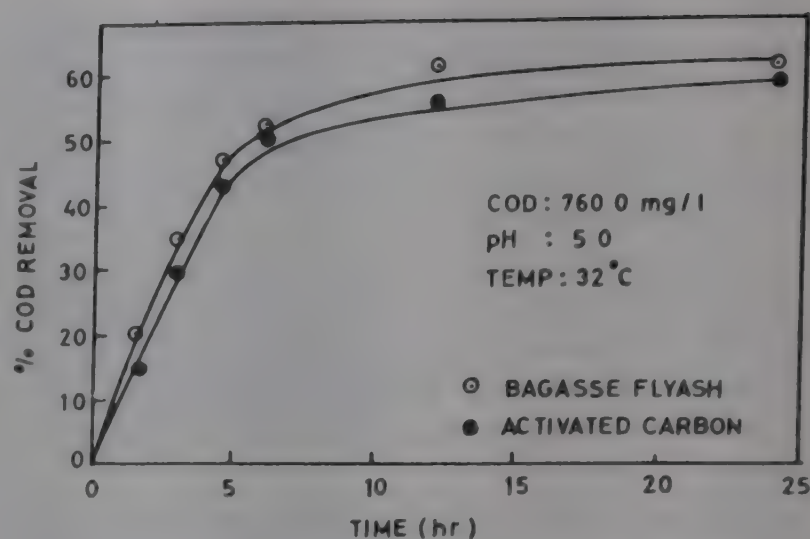


Fig. 3—Effect of contact time on removal of COD

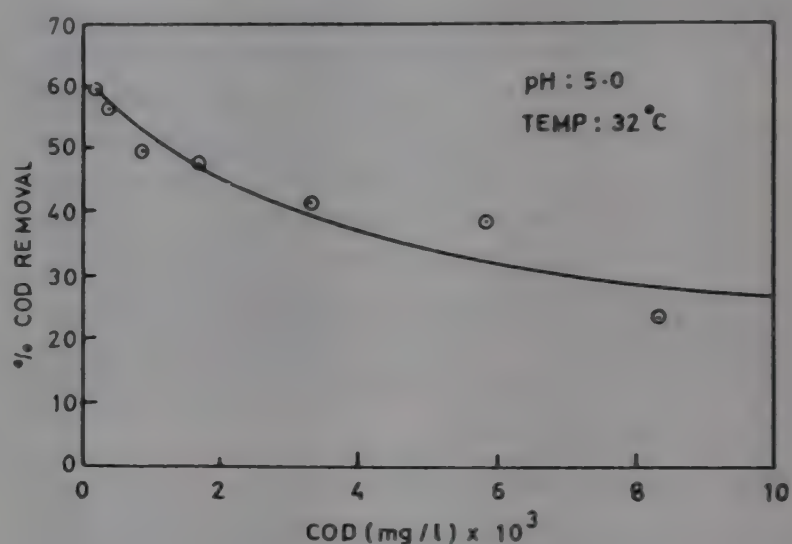


Fig. 4—Effect of initial concentration on removal of COD by bagasse fly ash

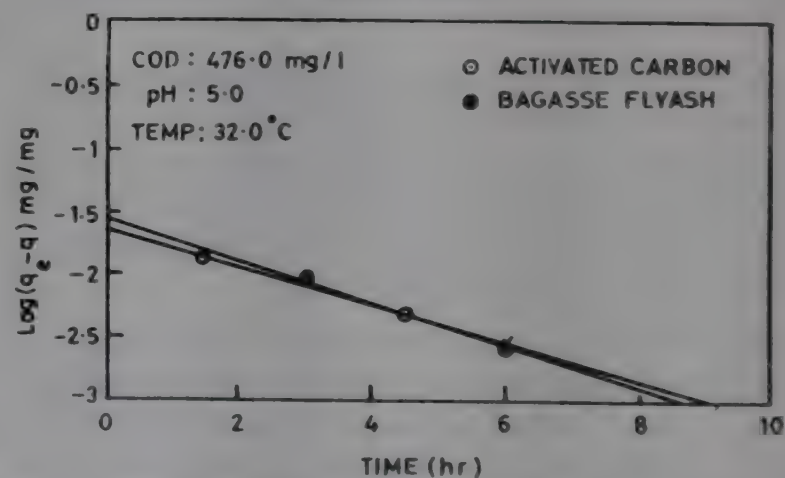


Fig. 5—Kinetics of COD removal by bagasse fly ash and activated carbon

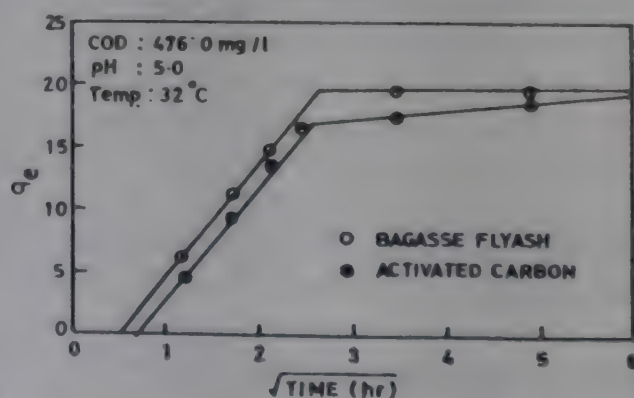


Fig. 6—Weber and Morris intraparticle diffusion plot for removal of COD

been reported in the range of 11-13 MJ/kg¹³. The bagasse fly ash can be utilised as fuel in the form of briquettes. A detailed work on utilisation of bagasse fly ash for fuel in the form of briquettes has been carried at the Alternative Hydroelectric Centre, University of Roorkee¹⁴. However, as the surface area of the bagasse fly ash is high, a further work is required for regeneration.

Conclusion

From the above it may be concluded that the bagasse fly ash is quite comparable to activated carbon in its adsorptive properties and therefore can be a good substitute of activated carbon for the treatment of wastewater from sugar mills.

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Table 6—Freundlich and Langmuir isotherm constants for bagasse fly ash

Adsorbent	Freundlich constant		Langmuir constant	
	a_F	$1/n$	Q_0 mg/g	b l/mg
Fly ash	0.269	0.57	166.67	6.0×10^{-4}
Activated carbon	0.190	0.72	125.00	7.3×10^{-4}

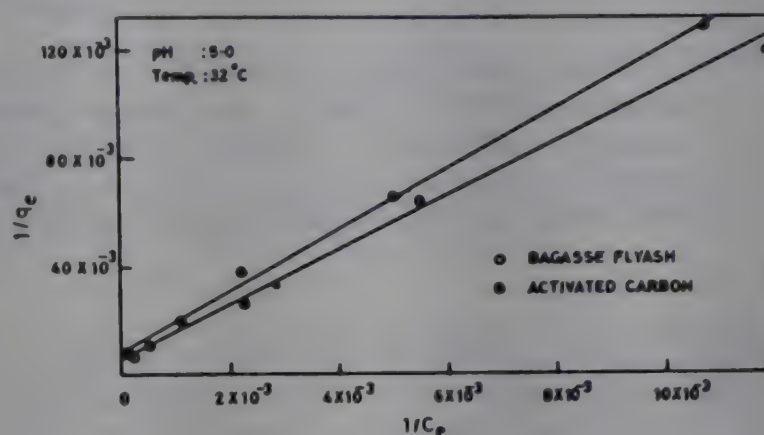


Fig. 7—Langmuir isotherm for bagasse fly ash and activated carbon

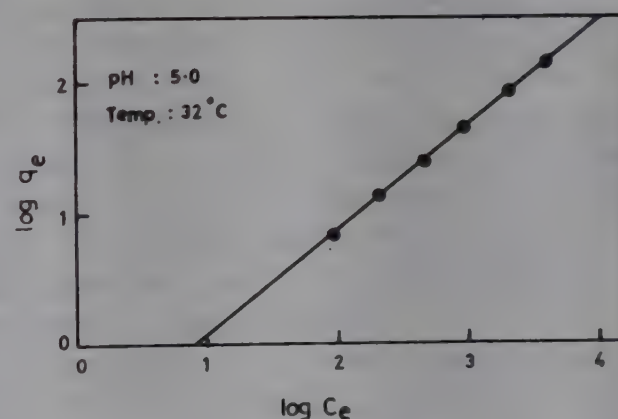


Fig. 8—Freundlich isotherm for activated carbon

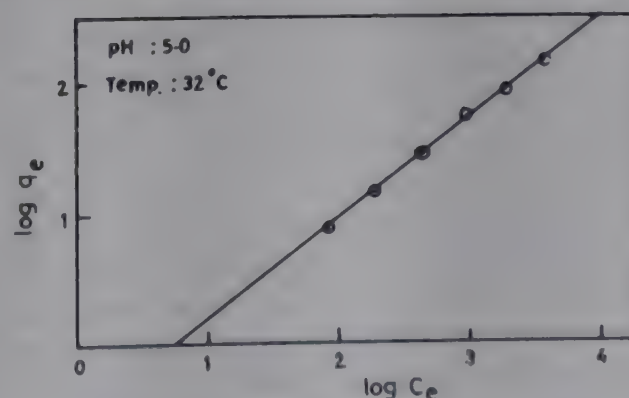


Fig. 9—Freundlich isotherm for bagasse fly ash

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Viscosity behaviour of vegetable gleditsia seed gum

Mrs Gohar Khan & M I H Farooqi

Phytochemistry Division, National Botanical Research Institute, Lucknow 226 001

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Recent trend in the utilization of vegetable gum is to use them in various combinations and concentrations. With this object in view physico-chemical characteristics of Gleditsia gum combination with microbial xanthan and carrageenan have been determined and reported in this paper. SEM studies showed a remarkable difference in structure of this gum and this may help to check adulteration. These observations may help the users of gum in various applications.

Vegetable gums, which are chemically carbohydrate polymers, have been used since time immemorial in various preparations of food but from the last several years many of these gums have become very important in several non-food industries also^{1,2}. The usefulness of all these gums based on their unique properties of gelling, thickening, sizing and stabilization in aqueous solution at low concentrations. More than four hundred thousand tonnes of various vegetable gums are being traded internationally every year for their uses in industries like pharmaceuticals, food, cosmetics, petroleum, explosives, textile, paper, etc^{3,4}. These gums of commercial importance include Ghatti gum, Gum-arabic, Tragacanth gum, Karaya gum and seed gums like Carob, Guar, Quince gum, Tara gum, Tamarind gum, Dhaincha and Cassia gums etc. Most of the vegetable gums are used in aqueous medium because their solubility in water is high. Recent trend in gum utilization is to use a mixture of two or more gums in water solution instead of using a single gum. This practice enhances the gelling or thickening and even adhesive properties of the final product along with a significant saving in cost. Thus a mixture of a seed gum and a seaweed gum like carrageenan, which is an important hydrocolloid may be more useful than the seed gum alone. In order to observe the behaviour of Gleditsia gum at different combinations and concentrations, the viscosity studies are reported in the present paper.

Gleditsia assamica (Fam.: Leguminosae, sub-family: Caesalpinodeae) is a tree of medium height. Gleditsia gums have already been patented in USA and France. The plants investigated were *G. amorphoides*, *G. triacanthos*, *G. ferox*, etc.

Material and Method

The *Gleditsia assamica* seed is dicotyledonous, flat in shape. The endosperm of the seed is responsible for the galactomannan gum. The hull and germ of the seed contain pentoses, mainly xylose. The endosperms of seeds were separated from seed coat and germs by the procedure of wet and dry milling at the laboratory with the help of grinders, mixers and various sieves⁵. The separated endosperms were crushed to coarse powder was further powdered in high speed hammer mill to different grades of gum i.e. 50, 75, 100, 120 and 150 mesh sizes.

For preparing gum solution, a weighed amount of gum was dissolved in minimum quantity of water and little methanol to check lump formation⁶. The suspension was transferred to a mixer using measured quantity of water. Then it was made up to a desired concentration and agitated vigorously till the solution became viscous and homogenous. The viscosities of the solutions were determined in cP with Brookfield Synchro-Lactic Viscometer Model RVT and LVT at 20 and 30 rpm respectively using spindle No. 1, 2 and 3. All viscosity determinations were recorded after hydration at room temperature (28-31°C). Moisture, protein, fatty oil, pentosan, fibre, ether extract, ash determinations were carried out according to standard methods. The gum was hydrolysed with N-sulphuric acid for 30 hrs at 100°C and after usual procedures PC of hydrolysate was carried out on a Whatman No. 1 sheet using solvent system n-butanol:acetic acid:water (4:1:5) and p-anisidine phosphate as spray reagent⁷.

Xanthan, carrageenan, carob, and guar gums were obtained from the manufacturers of Europe

and America. Milligrams of gum powder was mounted on brass stubs with double stick carpet tape and coated with gold-palladium in a Sputter coater. The surface of gum powder was checked after mounting to maintain uniformity. The gum samples were examined in a Jeol-JSM-35C Scanning Electron Microscope to an accelerating voltage of 15 KV and recorded on 120 mm ASA Camera. The interacted gum mixtures were acidified with 6N HCl to pH 2 and alkaline with 1 percent NaOH to pH 12. For complexing 0.3 g of AR Borax per 100 ml of gum solution was used after vigorous stirring for 5 minutes.

Results and Discussion

The *Gleditsia assamica* seeds have been found to be a potential source of seed gum as these contain about 40 percent of endosperm which is mainly responsible for water-soluble gum. The gum has been found to be of galactomannan type having galactose and mannose in the 1:4 ratio. The seed meal (60%) contain mainly pentosan of xylose alongwith approximately 25 percent of protein which may be utilized for poultry and cattle feed. The seeds are medium sized as the weight of 100 seeds is 24.0 gms. The seeds contain moisture 9.2 percent, protein 19.3 percent, pentosan 10.5 percent and fatty oil 3.9 percent. The average composition of the various seed component is given in Table 1.

The endosperm content is comparatively equal to commercial guar and carob gum which range from 35 to 42 and 42 to 46 percent respectively. Different grades of gum have been isolated by wet and dry processes. It has been observed that the wet process using organic solvents for isolating endosperm from seed coat (hull) and kernel (germ) afforded purer product than by dry process as given in Table 2.

The results reveals that the seed polysaccharide is galactomannan containing mainly galactose and mannose but dry process gum also showed traces of xylose. It is due to the fact that during dry milling of the seeds. Small portion of hull contami-

Table 2—Composition of *G. assamica* seed gums isolated by dry and wet process

	Dry process gum	Wet process gum
Yield on seed basis	28-30	39-40.3
Moisture	7.5	9.40
Protein	6.5	4.2
Pentosan	5.2	0.85
Ash	1.8	1.0
Acid insoluble matter	5.5	4.5
Loss of drying	9.5 (max)	9.5 (max)
Starch	Negative	Negative
Constituent sugars	Gal., Man, Xyl. (traces)	Gal., Man. (only)

nates with the endosperm, are, responsible for the presence of pentose in *Gleditsia* gum.

The gum isolated through wet process was dissolved in water and suspended impurities were removed by centrifugation. The gum was precipitated with ethanol and further purified by fractional precipitation. The purified gum was collected and dried into a white amorphous powder. The gum was hydrolysed with acid and after usual procedure. PC of hydrolysate showed it to be a pure galactomannan. No traces of xylose has been found in purified sample. The galactose content was found to be low (1:4).

The suspensions of different concentrations of the gum was prepared in water and viscosities were determined. It showed low viscosity upto 1 percent concentration and sharp increase in the viscosities with increase in concentration of above 1 percent as shown in Table 3.

The results from Table 3 has shown a valuable property of this gum of forming firm rubbery gel with biosynthetic gum like xanthan. Viscosity as high as 32,000 cP seems to prove its synergistic interaction with microbial gum. In view to observe the keeping quality or pseudoelasticity of the gum it was kept for eighteen long days and surprisingly it showed no degradation and fungus formation etc., but after this period of time degradation occur. The gum lose viscosity on keeping (Fig. 1). This type of characteristic has also been reported for carob gum diopersed at 85°C. This tendency

Table 1—Composition of the component of *Gleditsia assamica* seed

Seed part	Protein (N × 6.25) %	Ether extract %	Ash (sulphate) %	Moisture %	Crude fibre	Type of carbohydrate
Hull (38-42%)	15.4	0.6	4.9	5.65	31.40	Pentosan
Endosperm	4.25	0.5	1.05	9.4	1.45	Galactomannan
Germ (18-20%)	20.9	5.5	4.2	7.38	16.25	Pentosan

Table 3—Analysis of Gleditsia gum viscosity in combination with microbial gum

Gum Solutions	Viscosity in cP at room temp. 32°C
1st Day	
1% soln. of gum in cold	250
1% soln. after heating for 2 hrs.	750
Gum soln. + xanthan gum soln. (0.5:0.5) (Just after mixing, white coloured soln.)	22,500
After keeping mixture for 15-20 minutes	32,500
2nd Day	
After keeping in Refrigerator overnight	31,750
After heating on water bath for 1.5 hours (Temp. of soln. 80°C)	1,100
Keep the solution at room temp. for 1/2 hour (Gum soln. become cold)	31,750
3rd Day	
Viscosity at room temp. of the same soln. (No change in colour of soln.)	30,000
IV Day	
Soln. at room temp 31°C (Slight colour change)	5,500
VII Day	
Room temp. 30°C (same colour)	3,500
VIII Day	
Conditions of soln. as above	3,000
IX Day	
Room temp. 29°C (more change in colour)	2,000
X Day	
Colour of soln. more creamy (On 11th, 12th, 13th, 14th, 15th, 16th, 17th Days)	1,900-1,600
18 Day	
Soln. become concentrated (fully creamy)	1,500

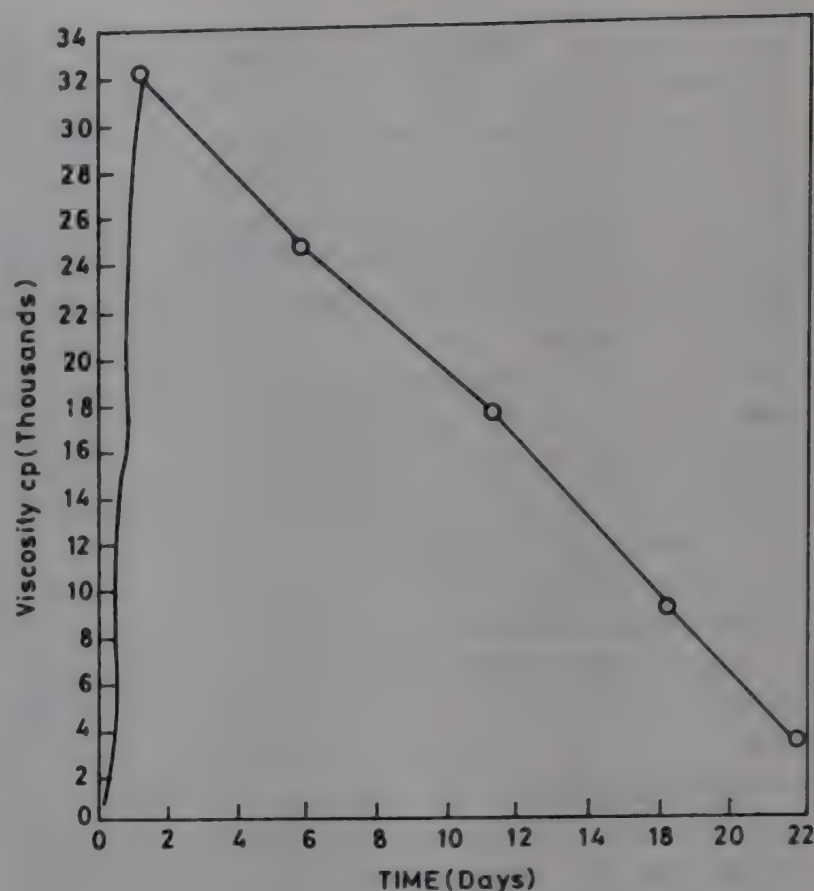


Fig. 1—Effect of time on viscosity

Table 4—Effect of carrageenan seaweed gum on viscosity of gleditsia

Sl. No	Gum Solution	Viscosity in cP
1	<i>G. assamica</i> 1% in cold	250
2	After heating on water bath for 2 hrs. (soln. hot)	750
3	Solution after cooling at room temperature (28°C)	350
4	Gum solution + carrageenan (0.5:0.5)	3,000
5	Solution of combination after 1 hour	9,000
6	Combination after 10 hours	11,000

can be checked by addition of preservatives. Gleditsia gum when treated with seaweed gum carrageenan in v/v basis. The following observations tabulated in Table 4 were recorded.

It was observed that the gum form complex with Fehling solution. The solution showed tendency towards gelling by the additon of borax. The crude gum powder gave thick solutions with water. With xanthan the gum completely changed its texture etc. This seed gum is dispersable in water at room temperature and vigorous stirring is required to prepare homogeneous solution. As the concentration of gum is increased it takes more time for complete dispersion 0.5 to 3.0 percent solutions of all grades of gum samples 50, 75, 100, 120 and 150 mesh size have been prepared and their viscosity studies were carried out. The results showed that the viscosity of gum increases with mesh size the gum. 2 percent solution of 50 mesh size showed viscosity of 650 cP followed by 75

mesh size, 825 cP, 100 mesh gum, 920 cP, 120 mesh gum, 950 cP, 150 mesh gum, 1000 cP. Like the commercial gums carob and guar. This gum also showed sharp increase in concentration. From 1 percent solution viscosity ranged from 200-250 cP which raised to 650-1000 for 2 percent solution followed by 825-1,900 for 3 percent and at higher concentrations it became gel. The viscosity behaviour of gum determined at different concentrations has been presented in Fig. 2.

Since the gum is non-ionic it showed the expected stability over wide range of pH. It showed maximum viscosity over pH 7.0. Viscosity increases to some extent on alkination but above pH 2, it decreases rather sharply. This type of change in viscosity with pH has been reported in most of the gums (Fig. 3).

Scanning Electron Microscopic studies were used to examine the characteristic distinct crystal-

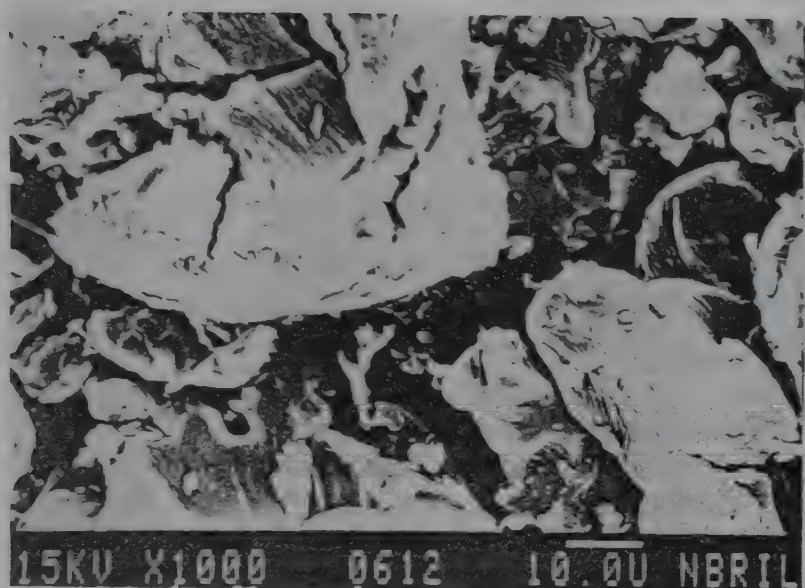
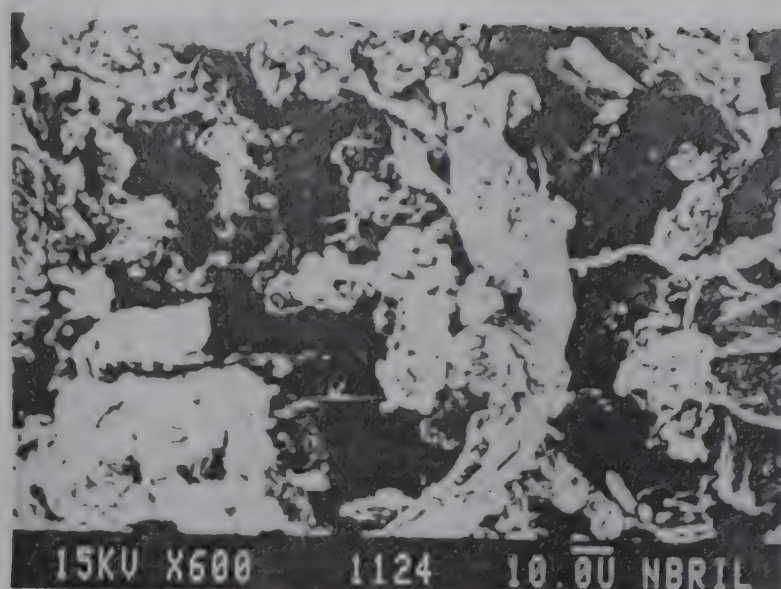
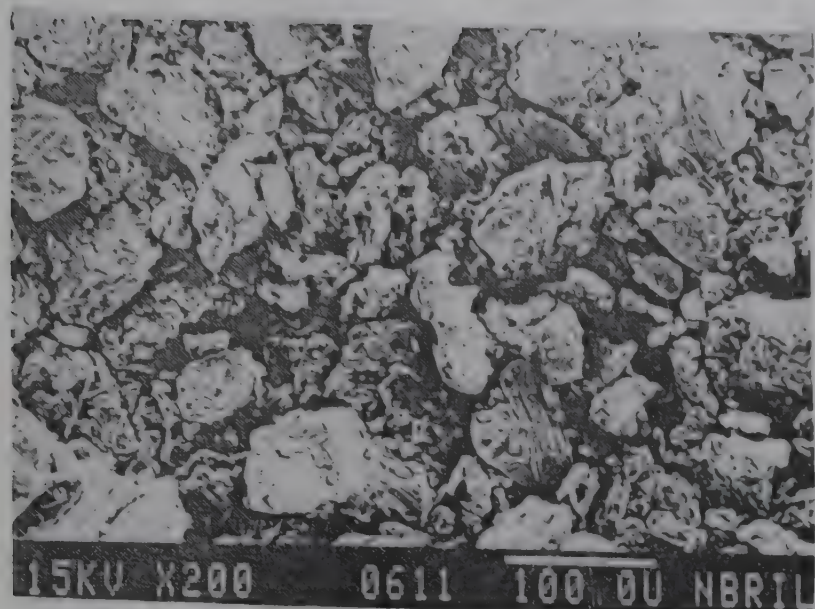


Fig. 4—Gleditsia gum at 200, 1000 and 6,000 magnification showing characteristic crystalline nature

Fig. 5—Gum in combination with xanthan

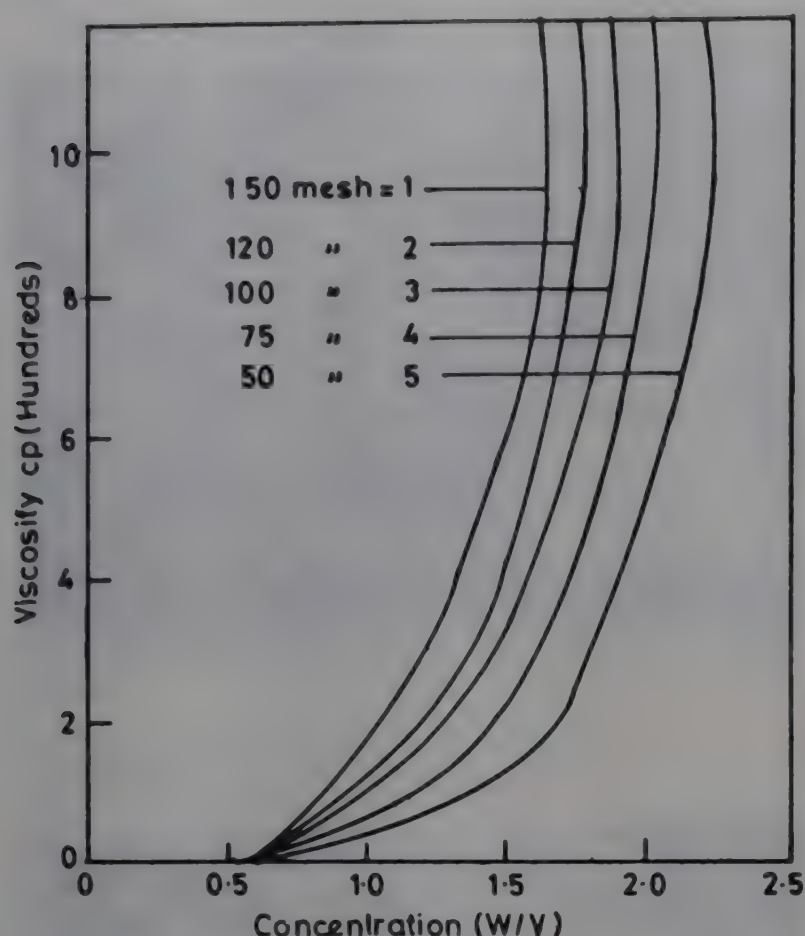


Fig. 2—Concentration versus viscosity of Gleditsia gum of 50, 75, 100, 120 and 150 mesh size dispersed at 30°C

line morphology of this gum alongwith two monosugars D-galactose and D-mannose. The gum samples were photographed at various magnifications starting from 200, 600, 1000 to as high as 6000. It was observed that Gleditsia gum at high magnification exhibited structure that was remarkably different from other gums like guar. (Fig. 4). Characteristic crystalline nature of these gums gave a quick physical identification. SEM studies also revealed that the distinct morphology of these natural polymers can be disturbed by adulteration as shown in (Fig. 5) by mixing Gleditsia with xanthan.

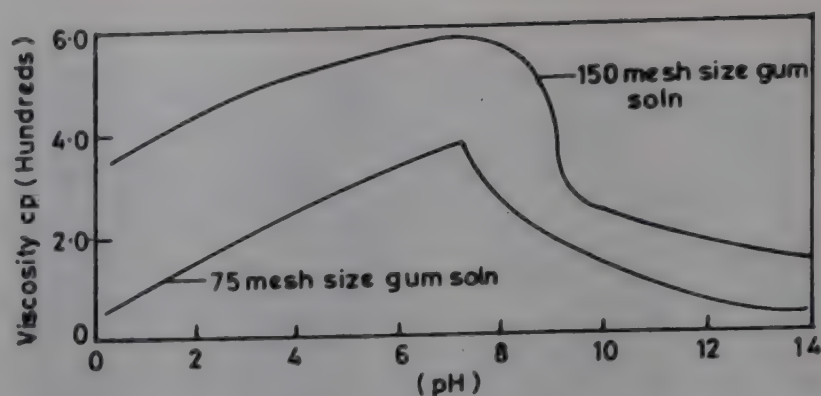


Fig. 3—Effect of pH on the viscosity of one percent 75 and 150 mesh Gleditsia gums dispersed at 30°C

Conclusion

From the above preliminary tests it has been shown that this gum has a potentiality to become a new source and like *G. triacanthos* etc. It can be used in cosmetic industry as a hair decrimper, in paper industry it can be used to give strength to the paper for making hand towels and tissue papers etc. If organized collection of Gleditsia gum could be done there is every possibility that this gum may be commercially exploited and can compete with carob (*Ceratonia siliqua*) gum.

Acknowledgement

The authors thank Dr P V Sane, Director, National Botanical Research Institute, Lucknow for his keen interest and encouragement in this work.

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Technology Up-date

Thin film solar technology

Chem Eng News, 72(4) (1994) 7

The US Department of Energy has announced an advance in thin film solar technology, based on an amorphous silicon alloy that will make it possible to generate solar energy at half the present cost.

Solar (photovoltaic) electricity now costs 25 to 50 cents per kWh, whereas with the new technology (in large-scale production) it will cost only 16 cents per kWh. Eventually, the cost could drop to as little as 12 cents per kWh.

The technology was developed by electronic engineer Subhendu Guha and coworkers at United Solar Systems Corp. (Uni-Solar), Troy, Mich.

Uni-Solar, a joint venture between Energy Conversion Devices Inc. (also in Troy) and Canon Inc., plans to manufacture solar panels based on the new technology at a plant in Newport News, Va., to be operational in 1995.

The solar panel developed by Guha's group has three amorphous silicon alloy layers, or cells, each of which converts a different region of the spectrum of sunlight into electricity. The panel has a stable solar conversion efficiency of 10.2 per cent a record for a thin film solar panel.

Stable efficiencies of more than 9 per cent have been achieved in other experimental thin film devices in the laboratory, but such devices have not yet been commercialized.

Thin film solar technology has been more difficult to develop than that based on crystalline silicon solar cells. Thin film panels can be manufactured at significantly less expense than crystalline silicon panels. Crystalline silicon devices are manufactured as small wafers that are then soldered together into larger modules, whereas thin film amorphous silicon can be continuously deposited directly on large sheets of glass or stainless steel.

Solar power based on the new technology would not be as cheap as coal and gas-fired electricity from power plants, which costs about 5 to 10 cents per kWh. However, use of solar energy in homes can reduce power distribution requirements and can decrease green house emissions caused by combustion-generated power.

Total chemical synthesis of taxol

European Chem News, 61(1606) (1994) 24

Two rival groups of US scientists are each claiming to be the first to have achieved the total chemical synthesis of taxol, the promising anti-cancer compound originally isolated from the rare Pacific yew tree.

The syntheses—though complex—are being hailed as significant, in that they open a chemical pathway for the production of both the natural product and a variety of designed taxoids.

The compound's scarcity has proved a major drawback in capitalising on its anti-cancer properties. Its structural complexity, with 11 stereocentres and a dense array of functionality, has taxed chemists for the past 20 years.

Now within days of each other, research teams from Florida and California have independently announced successful total syntheses of the drug.

Chemists at Florida State University led by Professor Robert Holton, has synthesised taxol starting from camphor. A US patent is pending.

Scientists at the Scripps Research Institute in La Jolla and the University of California at San Diego reported an alternative total synthesis which involves some 28 chemical steps of two previously reported intermediates (which also have to be prepared). However, the process is recognised for its flexibility which should allow the construction of numerous analogues.

These developments offer hope for the new analogues particularly for compounds with greater aqueous solubility (taxol itself is extremely insoluble in water). Whether they will lead to large quantities of taxol being made available or result in a decrease in costs remains unclear.

Holton received a US patent in May 1991 to partially synthesise taxol using, in part, a substance extracted from leaves of the English yew, a cousin of the Pacific yew. That process has now been industrialised.

Work continues to refine the total synthesis route.

New zeolite structures synthesized

Chem Eng News, 71(49) (1993) 8

Two new zeolites—with structures that could permit

more highly controlled catalysis in petroleum refining and petrochemical processes—have been synthesized and characterized by a joint research group at California Institute of Technology, Pasadena, and Chevron Research & Technology Co., Richmond, California.

The new zeolites, called SSZ-26 and SSZ-33 possess structures that effectively straddle those of ZSM-5 and zeolite-beta, two molecular sieves now in widespread industrial use for catalysis. The most prominent feature of SSZ-26 and SSZ-33 is the intersection of 10-ring and 12-ring pores to produce cages that are slightly smaller and slightly larger than the cages in ZSM-5 and zeolite-beta, respectively.

This feature of the new materials permits more highly controlled shape-selective catalysis in a number of refinery processes, such as isomerization and alkylation. The cages are accessible through both the 10-ring and 12-ring pores. In addition to differing geometry, the new molecular sieves are more stable than some currently used commercial zeolites and have good intracrystalline diffusion properties.

The new materials were synthesized with organic structure-directing agents. These are organic molecules that organize inorganic molecules around them during synthesis to yield the building blocks that eventually form the crystalline structure of the molecular sieves.

Interest in new zeolites has increased rapidly with the advent of new environmental regulations. Solid zeolite acids are being sought in labs around the world to eliminate some of the environmental threats posed by conventional strong acids. There is immediate interest in using SSZ-26 and SSZ-33 as hydrocracking catalysts. And tests for this use are under way at Chevron, the principal funder of this research.

Photorefractive polymers

Chem Eng News, 72(4) (1994) 24

Researchers at the University of Nebraska, Lincoln, have prepared photorefractive polymers that perform as well as, or better than, available inorganic photorefractive crystals. A material is photorefractive if its refractive index changes with the intensity of illumination. This property allows holograms—three dimensional interference patterns—to be formed directly in the material, without the need for chemical development. Photorefractive crystals potentially could be used in image processing, in optical data storage, and to correct image distortion. But the expense and difficulty of growing and preparing such crystals has held up their commercial application. Since polymers would cost less and could be readily fabricated in a variety of forms, scientists have been eyeing photo-

refractive polymers as potential substituents for crystals in future applications. But the performance of photorefractive polymers has not measured up to the crystals—until now. Physicist Stephen Ducharme and coworkers at Nebraska obtained their most encouraging results with a material that is a mixture of a 4, 4'-nitroaminostilbene-substituted electrooptic polymer and an organic hole-transport agent. Before such polymers can be incorporated into optical and opto-electronic devices, however, other materials properties will have to be improved.

Smallest metal pipes

Chem Ind, 24 (1993) 985

The world's nanotechnology laboratories are churning out a dizzying array of miniature marvels, from molecular chain links to threaded beads. Joel Schnur of the US's Naval Research Laboratory in Washington has added another: the world's smallest metal pipes.

Schnur has combined two techniques to make the pipes or 'tubules'. The first exploits a property of lipids, the fatty molecules which form the building blocks for biological membranes. In water, diacetylinic lipids tend to self-assemble into bilayers. When a solution of lipids in alcohol and water is cooled, a quirk of the lipids' chirality forces them to form into hollow tubules, about 0.5 μm in diameter and up to 1200 μm long.

However, as these tubules are essentially globs of fat with very little strength and are therefore too weak to be of much use. To make them stronger, the tubules are coated in metal, using a solution of palladium or tin ions as a catalyst. Schnur has so far made up to 70-90 μm -long metal cylinders with walls about 500Å thick.

Such cylinders are found very useful. For example, the team filled copper tubules with a viscous polymer matrix containing renilla, a bacterial antifouling agent, and then incorporated these into a marine paint. The renilla seeped out of the paint steadily for about three years: using current encapsulation techniques, it would all be gone within a month.

Another potential use is in cathode emitters which produce 'brighter' electron beams if their emitting surfaces are made up of an array of small hollow tubes. Schnur suspended nickel tubules in liquid epoxy resin, aligning them with magnetic fields and casting the resulting composite to get this effect.

Wear TV like a pair of glasses

Des News, 48(22) (1993) 28

Virtual Vision, Redmond, W A, has introduced tech-

nology to let one watch one game while attending the other.

The Virtual Vision Sport is a walkman-type device that displays a 60-inch (152.40 cm) colour TV image eight-to-15 ft (2.44-to-4.57 m) in front of a viewer. It is the device to use the viewer's peripheral vision, it is useful for more serious pursuits than watching sporting events. Other applications are: Surgeons could glance at data without moving their heads. Assembly workers can keep a drawing in view as they work. Hearing-impaired people could use it to read subtitle. Visually-impaired people with macular degeneration could use it for real-time viewing of such things as can labels in grocery stores.

The Sport consists of a pair of five-oz (0.14 kg) sunglasses connected to a belt pack the size of a portable stereo. The pack contains a TV tuner that transmits images to the eyewear, a rechargeable battery, and an interface system that connects to other equipment.

Within the eyewear is a miniature video display and a reflective optical system with a lens mounted slightly below the normal field of vision of the user's dominant eye. Locating the lens there makes it appear that both eyes are viewing the images. The lens bounces the video image from the display so it appears to be focused eight-to-15 feet in front of the viewer.

Design criteria were to make it lightweight, fashionable, comfortable to wear, and user-friendly, and to get the product to market in 15 months. The key enabling technology is an adaptation of the heads-up displays that fighter pilots use.

Sony, Olympus, and other developed technology that takes whole field of view, according to Brian Durwood, marketing vice-president. The average person only glances at TV rather than watching it exclusively, so the image was shrunk to 15 degrees of field of vision while giving the illusion of a full-size view.

Flywheel to power electric car

Des News, 49(1) (1994) 31

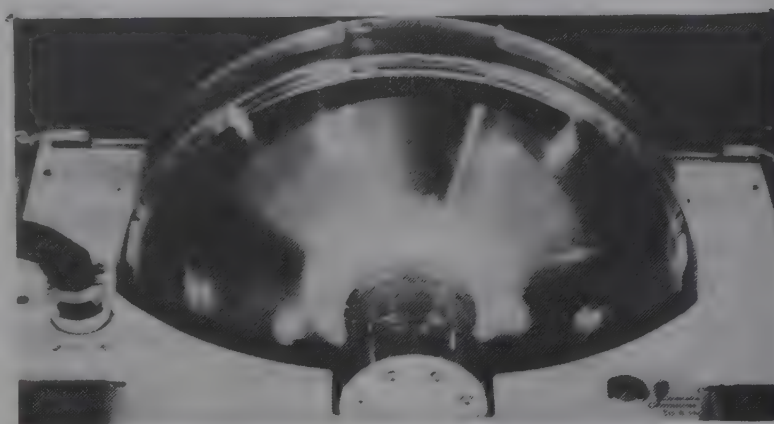
The flywheel batteries, which companies have been perfecting over 20 years, could enable electric vehicles to go as far and as fast as today's gasoline powered cars and no pollution.

Among the most recent developments is a prototype from American Flywheel Systems Inc. (AFS), Bellevue, WA. Built by Honeywell Inc. and sponsored by the Sacramento, CA, Municipal Utility District (SMUD), it is designed to comply with 1998 state requirements for a certain percentage of electric car sales.

Electric car owners could charge the battery overnight using a household 110 v outlet that generates



The walkman type TV wear glasses



Prototype flywheel battery

enough electricity to spin a pair of counter rotating rim wheels up to 200,000 rpm. The wheels are suspended by magnetic bearings encased in a vacuum housing. AFS believes the flywheel battery will provide at least triple the energy of the best lead acid batteries.

According to AFS chairman, E W Furia, flywheel technology will increase the range of electric vehicles from about 100 miles per charge today to more than 300 miles. Flywheel technology will also have other applications, predicted Winston Ashizawa of SMUD, "flywheel batteries will revolutionize not only cars, but also the generation and distribution of electricity."

The AFS-Honeywell development programme has plans to produce the first prototype flywheel batteries in 1994 for automaker evaluation and the first pre-production prototype batteries for the test car use in 1995. Prototype flywheel battery for electric vehicles will eventually let cars get up to 600 miles per charge, without the corrosion problems of lead batteries.

Ink jet for fast application of adhesives

Des News, 49(1) (1994) 37

Engineers at Asymtek Corp., Carlsbad CA, have applied ink-jet printing technology to the design of dispensers used in electronics assembly. This results new standards of speed, quality, and performance.

The company claims its new Dispense Jet more than doubles throughout rates to 20 dps. It includes closed-loop transducers, control electronics and control software. The inherent speed of the adhesive leaving the head allows the glue to be shot 'on the fly'.

The nozzle fits within a machine that serves as a horizontal XY platform that uses cables and stepper motors to move the nozzle head to various locations on an electronics board. Software activate the solenoid, whose impact creates a positive displacement causing the glue to be shot from the nozzle. The control electronics signal an air valve to pressurize the fluid source in the syringe. A closed loop volume sensor tells the electronics when the syringe is ready for the next shot.

To hold ICs and electronics on a circuit board during soldering, one has to be first glue everything in place. But often there are problems with board warpage. The Dispense Jet is insensitive to board warpage. In fact, the vertical motion and stopping of the dispense head that is required in conventional machines for the proper wetting of adhesive is completely eliminated, as is the requirement for surface height sensing input.

Dispense Jet also automatically dispenses various glue dot sizes within the same cycle to allow for different component sizes on the board.

Organic light-emitting diode

Chem Ind, 23 (1993) 929

The days of the semiconductor light-emitting diode (LED) may be numbered. Researchers at Stuttgart University have managed to make the first LEDs based on oligomers (small sections of a polymer)—an important step toward organic LEDs.

Organic LEDs would have several advantages over conventional semiconductor diodes: their light-emission properties could be tailored by chemical changes to the polymer, and they could also be made easily and cheaply into thin films and large-areas, flexible devices. However, there are still problems—the polymers used so far tend to be relatively unstable, have poor luminance and often require very large voltages.

The Stuttgart team made their LEDs using oligothiophenes (between four and seven thiophene unit

sections of polythiophenes) sandwiched between an indium-tin-oxide electrode and a thin layer of aluminium. They found that the higher-order oligomers worked best, producing current-voltage curves similar to those of semiconductor diodes (although not identical, probably because of disorder at the oligomer-aluminium interface). The diodes emitted orange-yellow light; the longer chains emitted redder light.

However, the team still has problems to overcome, especially with the stability of their LEDs. After 15 minutes' operation in air, the output tails off—possibly because the aluminium layer oxidises, increasing the diode energy gap; the oligomers in the film may also react with each other as they heat up.

New material for BOD analysis

A new dehydrated seeding material for BOD analysis has been developed by the Centre for Biochemical Technology (CBT), Delhi, in collaboration with Central Pollution Control Board, Delhi. The demand for consistency and high reproducibility has now been met with this newly-developed seed material that reduces the potential for error and makes BOD analysis an easy, clean and convenient laboratory test.

In the conventional method for BOD analysis, fresh sewage is used as a seed material. But its collection is time-consuming, the sewage collected is not a guaranteed source of microorganisms and variations in BOD tests occur owing to variations in the microbial population in the sewage samples obtained from different sources. As a result, it is difficult to obtain reproducible results for pollution control and industrial application. This has been overcome by the CBT seedling material where a uniform microbial population is present.

The seeding material is available as a stock item in a lyophilized form, which is convenient, cost-effective, safe and clean to use, covers a broad range of substrates (industrial effluents) and provides high reproducibility.

These special features of the seeding material will help in determining the strength of water pollution, waste loadings to treatment plants and evaluating the efficiency of such treatment plants with more reliability.

Detection of pollutants with xerogel

Science, 141(1907) (1994) 15

A form of porous glass that changes colour in the presence of certain gases could act as 'litmus paper' to detect pollutants. The glass, called a xerogel, contains vanadium oxide, and is pale pink. But in hydrogen sulphide the xerogel turns amber, in ammonia pale

yellow, in formic acid greenish brown, in acetic acid green, and in hydrogen purple.

The pores in the xerogel are only 10 to 20 nanometres across, just a few molecules across and much too small to be visible to the naked eye. They are created by suspending tiny solid particles, from a few atoms up to a micrometre across, in a gel, which is then dried. As the gel dries it shrinks in such a way as to leave the pores. This xerogel looks and behaves much like glass: it is hard and transparent, and can be polished. If it is baked at 1500°C, the pores disappear and the substance becomes almost identical to ordinary glass.

Albert Steigman and his colleagues at the Jet Propulsion Laboratory in Pasadena, California, and the University of California at Santa Barbara, made a xerogel containing silica and vanadium oxide as part of a study of electromechanical materials, which change their size when a current flows through them. The gel is made from water or alcohol with an alkaline gelling agent.

The colour of any substance is a consequence of the wavelength of light that it absorbs, which in turn depends on the shape and arrangement of its molecules. Before the xerogel has absorbed anything it is in a particular 'pseudo-tetrahedral' geometry. When molecules enter the pores, they react with the vanadium oxide. Due to geometry change, the vanadium begins to absorb light at a place it did not absorb before. The chemicals which the xerogel detects have to be more alkaline than the vanadium oxide. Some of the reactions seem reversible, including those with water and ammonia.

Now the team is investigating whether the xerogel can detect chemicals when mixed with other substances, and whether metals other than vanadium can act as detectors. Vanadium oxide prefers formaldehyde to water, and water to ammonia.

Removal of alkyl lead using blast furnace granulated slag

Indian J Chem Technol, 1(2) (1994) 121

The principal sources of tetraethyl lead (TEL) as pollutant have been identified as waste sludges from petroleum refineries and waste sludges as well as wastewater from manufacturing plants of alkyl lead compounds. The organic lead in wastewater from TEL manufacture has been reported to be in the range 126.7-144.8 mg/L. On account of its solubility in lipids, TEL is readily absorbed by the skin as well as the respiratory and gastrointestinal tracts. Its major portion accumulates in the brain due to a special affinity between organic lead and the lipid of nerve tissues.

TEL is more than hundred times as toxic as inorganic lead. The maximum allowable concentration of lead in effluents being discharged to a storm sewer or stream is 0.1 ppm.

TEL contaminated wastewater has been treated by various methods. However, the method developed by the School of Studies in Chemistry, Pandit Ravishankar Shukla University, Raipur, has been found to eliminate the entire presence of inorganic and organic lead from contaminated water by the simple contacting operation using blast furnace granulated slag. The slag is found to be capable of acting as electrochemical reductant. One gram of slag is found capable of removing 5.4 mg of alkyl lead (as TEL) in three days. The aqueous medium has been found to be more favourable compared to the gasoline medium in the removal process. The method is found to be simple in operation and inexpensive.

Semiconducting films for electronic devices

The National Physical Laboratory, New Delhi, has fabricated semiconducting polyaniline films that have vast potential applications in micro-electronic devices, light emitting diodes and field effect transistors.

The scientists fabricated the polyaniline-silicon polymer by evaporating polyaniline on silicon, while polyaniline was vacuum evaporated on glass plates coated with indium tin oxide and silver and a thin film of a metal such as indium, aluminium or tin deposited on this to form a metal-polyaniline-silver.

Recently, there has been an upswing in interest in electrically conducting polymers due to their vast potential applications in semiconductor devices. Conducting polymers are inexpensive, abundantly available and can be fabricated over a large area in the form of thin films. An added attraction is that their properties can be tailored to meet specific requirements.

Utilization of lime sludge for wastewater treatment

Indian J Chem Technol, 1(2) (1994) 115

Considerable quantity of lime sludge is produced in the acetylene generation process. The lime sludge which is a byproduct in the above process poses considerable problems in disposal. In the context of resource recovery of waste products, the utilization of lime sludge is of considerable importance. The Chemical Engineering Department of the Indian Institute of Technology, Madras, has attempted at utilizing this lime sludge for water and wastewater treatment, so that at least a portion of the lime sludge would be successfully utilized. Their results showed that the waste lime sludge can be used in water and wastewater treatment. In the water treatment, the percentage reduct-

ion in temporary hardness ranged from 11.6 to 90 per cent for a concomitant lime sludge addition in the range 1.5-7.5 g/l. In the synthetic wastewater treatment the orthophosphate content was brought down to 0.3 mg/l when the feed water ranged between 4.5-15.4 mg/l of orthophosphate with a lime sludge addition ranging from 0.4-16.0 g/l.

Colour removal from a dyestuff industry effluent using activated carbon

Indian J Chem Technol, 1(1) (1994) 13

Activated carbon adsorbents are extremely effective in removing colours from effluents from dye-manufacturing and user industries such as textile and paper units, which are some of the leading consumers of water.

The effluents from these industries contain small amounts of dyes which impart a colour to the waters and lower their aesthetic value.

Removing the dye colours from the waste waters is

more important than removing soluble colourless organic contaminants which increase the Biological Oxygen Demand (BOD) load.

It is normally difficult to remove dyes from the effluents since the dyes are biologically non-degradable and are stable under varying heat and light conditions. Hence, conventional primary and secondary sewage treatment systems used for waste waters are unsuitable, and scientists recommend a tertiary treatment system to remove the colour before discharging the effluent water into a municipal sewer or directly into a natural water system.

Adsorption systems based on granular activated carbon have been found to be ideal by the scientists of Department of Chemical Engineering, Indian Institute of Technology, Madras, and as they are economical and can be regenerated more than ten times.

The cyclic usage of regenerated carbon holds the key to the economic viability of activated carbon adsorption for waste water treatment.

Techno-economic News Round-up

CSIR sells technology

The Council of Scientific and Industrial Research (CSIR), India's premier research body comprising of 40 National Laboratories, has earned Rs 130 crore during the 1993-94 by way of transfer of indigenous technologies to the United States, UK, Germany, Canada, Switzerland, Australia and South Africa and to the industry in the country.

The technology transfer took place mostly in the areas of drugs, chemicals, catalysts, polymers, biotechnology and equipment and machinery.

During the current financial year, CSIR had received Rs 95 crore in foreign exchange in form of technology fee, royalties and consultancies and received Rs 35 crore by transferring CSIR's technologies and expertise to the industry within the country.

The institutes like the Indian Institute of Chemical Technology, Hyderabad; Central Leather Research Institute, Madras; National Chemical Laboratory, Pune; Central Drug Research Institute, Lucknow; and other were selling their expertise globally and all these efforts would help in transforming indigenous laboratory scale processes and technologies into commercially viable ones.

In the field of polymers the National Chemical Laboratory, Pune, has transferred a cost-effective process to make the polyurethane, used in waterproofing construction material, to Duckback and Co. Similarly, the Regional Research Laboratory, Jammu, was close to commercialise fibre-reinforced plastic gear castings for 2600 HP diesel locos. It was now being tested on railways and would replace costly steel castings.

The National Chemical Laboratory was using fibre-reinforced thermoplast for rotor fan for two- and three-wheelers and this was being commercialised by the Bajaj Autos in the country.

In the field of biotechnology a novel bioavailability enhancer, developed by the Regional Research Laboratory, Jammu, which reduces dosages of anti-tuberculosis and leprosy drugs, has been transferred to Cadila which was seeking international patent against the process. The use of this enhancer would reduce to dosages of the drug up to 50 per cent.

In the field of chemicals, the Indian Institute of Chemical Technology has transferred know-how for

making certain chemicals to Abbot Labs and the National Chemical Laboratory for Du Pont, GEC and Hoechst. The National Aeronautical Laboratory of Bangalore signed a contract with the Central Airport Authority of UK.

The Central Mining Research Station, Dhanbad, has strategic alliances with Kembla Coal of Australia where they would test a biological material for degasifying poisonous methane in coal mines. Similarly, SATARA of UK which gives quality certificates for shoes would have alliances with the Central Leather Research Institute which would do shoe testing and certification on their behalf.

Similarly, the Central Drug Institute has transferred a process for manufacture of centchroman, a non-steroidal oral contraceptive, to zymogenetics of USA who would test it for treatment of osteoporosis, an old age problem of bones. It was going to be the first drug against this disease.

CSIR has formulated an action plan to enlarge foreign business, initiate research and development in emerging technologies, new strategy for project identification and selection and patenting top class indigenous technologies internationally so as to help indigenous technologies to reach the stage of commercial applications and receive proper returns.

Indigenous technology for production of food-grade hexane

An indigenous technology for production of food-grade hexane, used in the extraction of vegetable oil from vegetable seeds, is being adopted by three public sector refineries and has saved the country Rs 30 crore foreign exchange by saving the import of food-grade hexane. The technology, developed by the Indian Institute of Petroleum (IIP), Dehradun, has been adopted by two public sector refineries namely BPCL, Bombay, and MRL, Madras, which are producing 25,000 tonnes per annum each of food grade hexane and the HPCL, Bombay, has agreed in principle to adopt the technology in next two years.

At present vegetable oils contain one per cent benzene against the world specifications of 40 parts per million, i.e. 0.040 per cent. The IIP technology reduces the benzene content to 0.05 per cent, very close to world specifications.

High quality food grade hexane, in which benzene would be in traces only, would not affect human health through the consumption of vegetable oils.

The technology has been developed in collaboration with Engineers India Limited (EIL) and it is based on 'liquid-liquid extraction technology' for the production of food grade hexane using sulpholane as a solvent. While the IIP has provided the basic know-how, EIL did detailed designing and engineering to make the technology a commercial success.

The food-grade hexane is used to improve the recovery of oil from the oil seeds. By normal extraction process only 25 to 30 per cent of oil is recovered from the oil seeds and therefore, manufacturers use food-grade hexane by which oil could be recovered by 95 per cent.

CECRI technologies through ITCOT

The Industrial and Technical Consultancy Organisation of Tamil Nadu Ltd (ITCOT), a joint venture of All India Financial Institutions and banks, is mainly concerned with the promotion of industrial development through consultancy, technology transfer and other related activities. It has been engaged by various organizations for preparing preinvestment feasibility reports for different projects/technologies, including those in the area of chemicals and electrochemicals, for their commercialization in Tamil Nadu and Pondicherry.

At the instance of ITCOT, the Central Electrochemical Research Institute (CECRI), Karaikudi, entered into an agreement with the firm, under which it will market the technologies developed by CECRI in Tamil Nadu and Pondicherry.

TIFAC-CSIO collaboration

The Technology Information, Forecasting and Assessment Council (TIFAC) has been established by the Government of India as a follow-up of the Technology Policy Statement of 1983 and on the recommendations of the Technology Policy Implementation Committee. The basic objectives of TIFAC include generation of technology forecasting (TF) and technology assessment (TA) reports in the key areas of technology, and establishment of an on-line, interactive, decentralized but nationally accessible computer-based technology information system (TIFACLINE) on processes, products, markets, and experts, etc. involved with the chosen technologies. And the Central Scientific Instruments Organisation (CSIO), Chandigarh, has been playing a prominent and multi-dimensional role towards the promotion and growth of indigenous instruments industry in the country.

Keeping in view the roles of TIFAC and CSIO, particularly with regard to instruments industry in the country, a new joint mechanism, TIFAC-CSIO Board has been established. The board endeavours to accelerate the growth of indigenous instrument industry in the country and direct the instrumentation activity so as to focus on development of specific commercializable instruments and systems having a larger impact on India's economy.

As a part of these efforts, the TIFAC-CSIO Board has taken up the task of creating and updating the database on different aspects relating to instrumentation and instrument industry.

RRL consultancy for cement plant

The Regional Research Laboratory (RRL), Jorhat, has entered into an agreement for a turnkey consultancy assignment worth Rs 5 million with M/s Karbi Anglong Chemicals Ltd (KACL), for a 30,000 tonnes per annum capacity Vertical Shaft Kiln (VSK) cement plant at Karbi Anglong. The project is likely to cost around Rs 90 million. M/s KACL took this decision on the basis of a techno-economic feasibility report prepared by the laboratory.

RRL will provide to the firm technical details and project engineering and technical services, advice and assistance at different stages of implementation of the project. It shall also provide training to chemists and technicians for operation of the plant. The work is expected to be completed within a period of two years.

This is going to be the biggest mini-cement plant based on the RRL technology in private sector in the whole of north-eastern region. The first two VSK cement plants of 7500 tonnes/annum capacity were set up at Guwahati and Lanka, Nowgong. Both these plants are in production. Throughout the country, 29 parties are reported to be in continuous commercial production based on the RRL-Jorhat technology.

RRL-Jorhat has developed the VSK technology for different plant capacities ranging from 6000 to 30,000 tonnes/annum. The cement plants based on this technology are low capital intensive, having a short gestation period resulting in quick return on investment. These plants have also helped in utilization of small deposits of limestone and cutting on transport costs as the product can be consumed locally. This technology is of particular interest to young entrepreneurs with limited financial resources.

RRL-Jorhat is also exploring the possibility to export this technology abroad. Meanwhile, the United Nations Centre for Human Settlement (UNCHS) has shown considerable interest in this technology and sponsored a visit of RRL scientists to Iran in this connection.

National Unity Award '94

Novoflex Cable Care Systems, a Calcutta-based company pioneer in manufacture of world-class import substitute wiring accessories, electrical installation materials, electronic component parts have been presented the above award in recognition for outstanding services, achievements and contribution to the Nation on the 24th Jan '94 in New Delhi on the occasion of the National Conference of Economic Development. Novoflex have over 20 years experience in the field. They are established source with proven record of dependability and consistency in quality.

NRDC Republic Day Awards

The National Research Development Corporation (NRDC) takes pleasure to announce 1994 Republic Day Awards for innovative inventions under its Invention Promotion Programme. The Prize Award Committee has recognised developments and inventions in the following key areas of national importance.

Chitra artificial heart valve prosthesis

S/Shri G S Bhuvaneshwar, O S Neelakanthan Nair and C V Murlidharan of Sree Chitra Tirunal Institute for Medical Sciences and Technology, Trivandrum, have been jointly awarded a sum of Rs 75,000 for the development of Chitra heart valve prosthesis—the mechanical heart valve used for the replacement of mal-functioning heart valves in the human body. The Chitra heart valve has been cleared, after multi-centric clinical trials for wider use. The performance of the valve is comparable or even better in comparison to the currently imported valves. The availability of indigenously developed heart valve will save valuable foreign exchange.

Automatic self-adjusting spanner/wrench

S/Shri Chandrakant V Solanki and Hitendra V Solanki, Partners of M/s Solsons, Ahmedabad, have been jointly awarded Rs 75,000 for designing and developing a unique automatic self adjusting spanner/wrench. This unique spanner is already being exported to a number of developed countries.

Passive radiant cooler for very high resolution radiometer of INSAT satellite

S/Shri Prakash P Gupta and S C Rastogi of ISRO Satellite Centre, Bangalore, Dr (Mrs) Indira Rajagopal of National Aeronautical Laboratory, Bangalore, and Dr Ajay Kumar Saxena of Indian Institute of Astrophysics, Bangalore, have been jointly awarded a sum of Rs 40,000 for development of spaceworthy passive radiant cooler which forms a part of the very

high resolution radiometer used for meteorological application on board satellites. The passive radiant cooler houses infra red detector and infrared channel optical elements and cools and maintains the temperature at 105 K utilising deep space as the heat sink.

Mini crane for building construction

S/Shri J P Kaushish, Bhagwan Das, S K Saini, D K Gautam and Mahendra Pal of Central Building Research Institute, Roorkee, have been jointly awarded Rs 30,000 for designing and developing a mini-crane of unique design for use in residential buildings, construction sites where light loads of 50 to 500 kg are required to be lifted and suitably placed for construction work.

Air plasma cutting welding equipment

Shri Gerrard R Thomas, Managing Director, M/s Gerrard Plasma Systems Pvt Ltd, Bombay, has been awarded a sum of Rs 25,000 for development of air plasma cutting system. The novelty of the system involves replacing inert gas by air and using either hand held or machine mounted torches connected to a self-contained power source incorporating an integral air compressor.

Development of beryllium components

S/Shri Nagaswami Sivasubramanian, Beant Prakash Sharma and Ved Prakash Sharma of Bhabha Atomic Research Centre (BARC), Bombay, have been jointly awarded a sum of Rs 25,000 for the development of the process for production of beryllium from Indian beryl ore and manufacture of beryllium components and beryllium alloys for space and military applications.

Air plasma cutting-cum-TIG-cum-MMA welding system

Shri Hughen Thomas, Chairman and Managing Director, M/s Plasma Cutting Equipment Pvt Ltd, Pune, have been awarded a sum of Rs 25,000 for the development of air plasma cutting-cum-TIG-cum-MMA welding system. The applicant has combined 3 modules, viz. (i) Air plasma cutting system, (ii) DC tungsten inert gas (TIG) welding system, and (iii) DC electrical welding system, into one machine. The novelty of the design lies in the unique geometry of the torch and in the fact that the arc constriction is done by special devices located at strategic positions in the torch.

Building block technique for solid polymer propellant grains

Ms Lalitha Ramchandran, S/Shri S K Athithan, P M

Varkey and Dr V N Krishnamurthy of Vikrak Sarabhai Space Centre, Thiruvananthapuram, have been jointly awarded a sum of Rs 25,000 for the development of a new technique for making large propellant grains of any shape and size using elementary propellant blocks with limited infrastructure. It is a cost and time effective process for repairing any defective grain especially in the large SLV motors.

Spark gap for protection of series capacitors in 220 kV transmission systems

Dr S C Gupta and S/Shri R Rajaraman and K R Sulaiman Sheriff of M/s Bharat Heavy Electricals Ltd, Corporate R&D Division, Hyderabad, have been jointly awarded a sum of Rs 15,000 for the development of spark gap for protection of series capacitors in 220 kV

transmission systems. Series compensation schemes are used to improve the voltage in transmission and distribution system. This non-self extinguishing type spark gap employs a three electrode system and has been supplied to various electricity boards.

Boron technology

Dr C K Gupta and Shri D K Bose of Bhabha Atomic Research Centre (BARC), Bombay, have been jointly awarded a sum of Rs 15,000 for the development of the process for the manufacture of boron carbide and production of elemental boron therefrom, development and fabrication technique for various boron carbide composite like aluminium-bonded boron carbide composites (Boral), boron carbide silicon rubber composites (Bocarsil) and polyboron shapes.

R&D Meetings

PLASTINDIA '94

The Plastic Foundation, Bombay, a national body of major trade and professional institutions of plastics industry in India, organised this exhibition and conference at Pragati Maidan, New Delhi during Feb 26-March 4, 1994 on a grand scale. The exhibition spread over a number of halls of the Pragati Maidan had exhibitors from India and abroad. Some of the major participating exhibitor groups were on: raw materials; speciality chemicals, master batches, additives, colourants, fillers and reinforcements; process machinery; ancilliary equipment; recycling; printing and decoration of plastics; plastic products, semi-finished and finished goods; moulds and dies; quality control instruments; and testing equipment. New generation injection moulding machines were great attraction. The buzz words were intelligent process control, multi-processor, closed loop control graphic capabilities. Klockner Windsor drew large numbers of enquiries on their displays. Recycling machines, plastic processing and printing equipment drew attention of many looking for employment opportunities.

The Conference going concurrently with the exhibition provided a vast scenario of the plastics in the world. There were four technical sessions: (i) Materials—A New Era; (ii) Machinery and Moulds—The Vital Link; (iii) Products/Market-Challenges & Opportunities; (iv) Plasticulture—A Promising Future. The experts who gave very illustrated deliberations were from USA, the Netherland, Switzerland, UK, Germany, France and of course from India. Some of the important lectures were on: (i) World prospective of plastic industry in the 1990s, (ii) European competitiveness in global market, (iii) Automation in plastics processing, (iv) Temperature control of injection moulds by fluids, (v) International development in recycling equipment, (vi) Market and applications—worldwide trends, (vii) Drip irrigation, (viii) International status of plasticulture, and (ix) Agriculture & horticulture films.

The concluding address was given by K K Mathur, Secretary, Department of Chemicals & Petrochemicals, Govt. of India. He lauded the role of plastic industry as low-energy consumer, environment friendly and employment generating sector. He made a call for making plastic revolution and exhorted the industry

to work out a strategy for it. He promised all help from the government for this.

WIPO Asian Regional Seminar on the use of Patent Information by Industry

The seminar was organised by World Intellectual Property Organization in cooperation with the Department of Industrial Development, Ministry of Industry, Government of India and Confederation of India Industry with assistance of the United Nations Development Programme at New Delhi during March 16-18, 1994. The Union Commerce Minister Pranab Mukherjee while inaugurating the seminar said the Government of India had decided to form an apex level advisory committee of users and providers of patent information services to look into patent related issues which will be chaired by users of these services. The honourable minister clarified the misconception that India had no proper Intellectual Property Rights Regime, when in reality 95 per cent of the IPR Regime in India was in conformity with international standards. He called upon the Indian agencies like NIC, CSIR, ASSOCHAM, FICCI and CII to coordinate their working and spread the message of importance of patent information in serving the needs of technology to all parts of the country.

In the key note address Dr Arpad Bogsch, Director General WIPO emphasized the need for making patent information systems user-friendly. The CII President Jamshyd N Godrej in his welcome address said that in the business world technology supremacy was the key to success and it lies with the patent information systems, the store houses of technology information, innovations and inventions. The seminar was attended by scientists, technocrats, industrialists and patent information providers from India and abroad. There were fruitful discussions between generators of technologies, providers of such informations and the users in the industry. Top patent information systems like European Patent Office (Munich), WIPO (Switzerland), US Patent & Trademark Office (Washington), Japanese Patent Office (Tokyo), Chinese Patent Office (Beijing), Indian Patent Information System (Nagpur) and vendors like Derwent, DIALOG gave illustrated demonstrations of the facilities and services they can render to the users.

The CII Economic Committee chairman Mr R C Bhargava gave a broad perspective of patent information needs of Indian industry. He made very useful suggestions for setting up a modern industrial property system and an integrated computerised patent information system for the Indian industry. These are summarised as follows:

1 A user-friendly information system with easy access, efficient and speedy search, reliable and accurate performance, at an affordable cost.

2 The information system to facilitate accessing of the abstract/first page database on state-of-the-art technologies and the most recent technology by trained searcher/examiners.

(a) Un-examined, patent/utility model applications.

(b) Examined, patent/utility model applications.

(c) Other technology innovations.

3 Selective search of database to provide an insight to the extent of development in specific field. Scope/avenue open for investigation or innovation.

4 Selective information package to decide research priority/strategy and investment opportunity.

5 Information available both on-line and off-line, through a single reference window, at widely dispersed locations in the country.

6 User-friendly training package for training of prospective user, database searcher/examiner and operator. Regular videotext broadcast through TV for general public. Video/audiovisual training package for learners and students.

7 PIS integrated through IPO's and other offices, to facilitate industry wide access.

Off-line services on queries received through other media.

Availability of CD-ROMs on India patents at early date.

8 Establish linkages with international/regional patent offices for accessing their database on patents.

9 PIS should establish linkages with ASEAN countries and network available databases for access.

10 Industry being the major user, access to database should be available through industry associations and other technology information centres.

11 Access should also be available to R&D establishments, consultants/inventors and practitioners at affordable costs.

12 Spread awareness on patent systems and services established in India, through organised workshops and seminars.

Role, functioning & services offered at PIS and the rates charged for such service must be duly publicised.

Selective dissemination of information to all users.

13 Need for Advisory Committee to strengthen Patent Information Services, with industry participation and other stakeholders.

Industry support for:

Development and marketing of patent of patent services in India.

Support on development of software/database and CD-ROM.

Participation in search and dissemination of patent information.

AUTOFACT '93

AUTOFACT '93 in Chicago, III, USA ended the year—on a high note, attracting a total attendance of 19,679—maintaining the event's status as the premier exposition and conference for computer applications in manufacturing.

AUTOFACT offered a total solutions approach by showcasing the most advanced technologies in both design and production, said Nancy Berg, director of expositions for the Society of Manufacturing Engineers (SME), the event's manager and producer. This year's event featured a wide diversity of technologies, yet the focus remained on helping manufacturers to find software and hardware solutions to integrate their design and production processes.

The 3-day AUTOFACT '93 Exposition took place Nov. 9-11 while a 5-day Conference ran concurrently Nov. 7-11. The 125,000 sq ft exposition featured more than 270 exhibits including over 60 first-time AUTOFACT exhibitors. Also new to the exposition were two technology pavilions devoted to plant engineering and networking.

During its 16 years history, AUTOFACT has established itself as a leading forum for new product introductions related to computer aided design (CAD), computer aided manufacturing (CAM), computer aided engineering (CAE), and computer integrated manufacturing (CIM). AUTOFACT '93 was no exception with the unveiling of new software products, and advanced equipment such as 3D digitizers, rapid prototyping machines, and high speed plotters.

This year, both exhibitors and vendors increased their emphasis on improving data management to better support concurrent engineering efforts. Also noticeable was the trend toward incorporating virtual reality into the design process as many exhibitors featured powerful simulation programs for engineers and designers who need improved ways of evaluating the manufacturing of all products.

This pursuit of improved technology was also the subject of the AUTOFACT '93 opening keynote session during which Dr. John Gibbons, director of the

US Office of Science and Technology and assistant to the US President, applauded manufacturers who are striving toward improved competitiveness with new products and services.

Gibbon's address reflected the AUTOFACT Conference theme which focussed on how to manage the transition to integrated manufacturing. More than 100 case studies, hands-on workshops, and interactive sessions provided practical information on transitions facing manufacturing companies. Topics ranged from rapid prototyping, flexible manufacturing cells, product data management, and advanced CAD/CAM issues, to the subjects of dual use technology and the client server environment.

Just as AUTOFACT '93 ended the year in style, show organizers are planning to kick off 1994 with even higher expectations. A second event has been added to the schedule, creating an AUTOFACT series in 1994.

Also planned for next year is AUTOFACT '94 Exposition and Conference in November at the Cobo Convention Center in Detroit, Mich. The AUTOFACT '94 Conference running Nov. 13-17 and the AUTOFACT '94 Exposition running November 15-17.

Finishing '93

Whether it was understanding the latest painting and coatings systems and applications, complying with EPA VOC regulations, solving an abrasive finishing problem, or just reducing overall costs, manufacturing professionals could find it there, in this event.

The triumvirate of expositions-Finishing '93, International Grinding, and Deburring & Surface Conditioning 'covered it all' and drew 5,712 manufacturing professionals. Sponsored by the Society of Manufacturing Engineer (SME), these events were held recently at Cincinnati's Dr. Albert B. Sabin Convention Center. SME, headquartered in Dearborn, Michigan is an international professional society dedicated to advancing scientific knowledge in the field of manufacturing engineering and management.

Some 252 exhibitors, occupying 59,112 net sq. ft., of exhibit space demonstrated spray finishing, surface preparation, powder and liquid coatings, material handling systems, polishing and buffing, recovery systems, curing, and waste management equipment.

Also displayed were CNC grinding machines, process control equipment, ceramic grinding, inspection gages, deburring, superabrasives, and blast finishing. Fifty four of the 1993 exhibiting companies reserved over 16,600 net sq. ft. for the next show in September 19-21, 1995.

For the first-time, attendees voted for the best exhibits in three categories: Most Technically Informa-

tive Exhibit: Wagner Systems, Inc., Glendale Heights, Ill; Most Impressive Exhibit or Display: Nordson Corporation, Amherst, Ohio; and Most Promising Company of the Future: ABB Paint Finishing, Troy, Michigan.

The concurrent conferences drew some 600 attendees-Finishing, 323; the 5th International Grinding, 178; and Deburring & Surface Conditioning, 76.

The accompanying Finishing conference, sponsored by SME in cooperation with the Association for Finishing Processes (AFP/SME), had sessions on environmental compliance, powder coating, systems design, quality, and liquid coatings. The 5th International Grinding Conference focussed on the technology and management of production grinding processes, materials, and technology. Deburring and Surface Conditioning session topics were mass finishing, special processes, blast finishing, finguring and robotic/mechanical processes. The grinding and deburring events are sponsored by SME in cooperation with the Machining Technology Association of SME (MTA/SME).

In addition to the exposition and conference sessions, the Finishing Roundtable was a source of information for the media. Twelve industry experts addressed a number of questions covering environmental compliance, emerging technologies, and industry specific issues. Roundtable Moderator Jack Stauffer, past president of AFP/SME, introduced the panelists: Bob Collins, Metal Finishing Services, Inc.; Peter Lambert, Nordson Corporation; Ron Farrell, Ferro Corporation; Marc Fooksman, Gema-Volstatic; Robert Grear, Navistar International Transport Corp. (ret.); Steve Kiefer, Morton International; Bill Lauersdorf, DeVilbiss Ransburg; Bob Lindrud, Nordson Corporation; Gregg Matschke, Binks Manufacturing Co.; Phil Phillips, Chem Quest Group; Renee Shreves, Miles Corporation; and Gary Sweet, Allied Polymer Systems, Inc.

National symposium on catalysis

The Catalysis Society of India (Bombay chapter) is organising the 12th National Symposium on Catalysis, at Bhabha Atomic Research Centre, Trombay, during 19-21 December, 1994. The symposium aims at covering all the important aspects of catalysis—fundamental, applied as well as engineering.

Contact address:

Dr. N.M. Gupta
Convenor, CATSYMP-94
Chemistry Division
Bhabha Atomic Research Centre

Trombay, Bombay 4000 085, India

Tel: 5563060

Telex: 011-71017 BARC IN

FAX: 91-22-5560750

E-mail: manohar @ mangnun, barct lernet. in

SME's Finishing Events 1994

Society of Manufacturing Engineers (SME), headquartered in Dearborn, Michigan, USA is an international professional society dedicated to advancing scientific knowledge in the field of manufacturing engineering and management. Founded in 1932 SME has more than 75,000 members in 68 countries and sponsors over 325 senior chapters and 220 student chapters worldwide.

Finishing schedule for 1994 (from June to November), sponsored by the (SNE) and the Association for Finishing Processes of SME (AFP/SME), is as follows:

June

7-8	Industrial painting processes	Toronto, ONT
9	DOE for liquid coating applications	Toronto, ONT
14-15	Developing effective powder coating Appl	Chicago, IL
16	Advanced powder systems trouble-shooting	Chicago, IL
TBD	Furniture finishing	Grand Rapids, MI

August

22-23	Spray application methods for	LA
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	powder coating	
24-25	Optimizing profits in a powder coating job	LA

September

13	Fund of liquid paint formulation for paint appl	Cincinnati, OH
14-15	Liquid paint systems design	Cincinnati, OH
12-13	Spray application methods for powder coating	Amherst, OH
14-15	Spray application methods for powder coating	Amherst, OH
20-21	New applications of powder coating for auto	Detroit, MI
27-28	Dev effective powder coating appl	Toronto, ONT
29	Adv powder systems trouble-shooting	Toronto, ONT

October

18-19	Polyurethane coatings	Nashville, TN
18-19	Environmental compliance for the coating ind	Cleveland, OH
TBD	Pint stripping of large products	TBD
TBD	SPC for paint lines	East/South
TBD	Spray application methods for powder coating	Chicago, IL

November

15-16	Industrial painting processes	Nashville, TN
8-9	Furniture finishing	High Point, NC

For more information on the above programme, contact Maria Conrado at SME International Headquarters, P.O. Box 930, Dearborn, Michigan 48121-0930 USA, (313) 271-1500, ext 376. Fax (313) 271-2861.

Technical Literature

Technology in Indian High Pressure Boiler Industry (Govt. of India, Department of Scientific & Industrial Research, New Delhi 110 016), 1993, pp. 165

With the Government's new policies to give Indian industry a boost to bring it at par with international scene, a quantum jump in energy requirement is envisaged and thermal power plants are expected to be main stay of India's energy needs for at least next couple of decades. The need arises to apprise the prospective users—both the entrepreneur and the engineer to get enough requisite information on the basic aspects of the high pressure boiler industry in India, i.e., selection, design, construction, erection, testing and operation with special emphasis on boiler design based on specifications of Indian coal. With deterioration in coal quality over the years, the generation capacity of old units have also decreased considerably and calls for technological inputs to make the units economically viable by giving full capacity utilisation.

The Report is a complete and lucid work on the subject and gives requisite information. It is a complete guide to the design engineer to select the unit based on the load requirements, type of fuel available, operating parameters, statutory requirements of pollution control on particulate and gaseous emission, method of refuse disposal, etc. The chapter on specification of Indian coal with detailed typical analysis of fuels is very informative and will enable the engineer to select the right type of the boiler and its auxiliaries.

The list of sub-suppliers and foreign collaborators will help the entrepreneur choose the best for his plant. Another critical aspect of high pressure boiler industry is the selection of right material for manufacture of equipment for high pressure and temperature service and use of internationally acceptable standard engineering practices during manufacture, testing and erection stages. The relevant specification grades, physical and chemical properties of almost all materials used are a great help to the design as well as maintenance engineers.

Construction details of major items, viz. boiler furnace water walls, superheaters, reheaters, economisers, fans and drives, electrostatic precipitators or bag filters are quite elaborate. Chapter on technology absorption, R&D efforts, indigenisation efforts, etc. is very informative both for new units and modification

of old units. State-of-the-art technologies are being developed to counter the effect of poor Indian coal of high ash, abrasive and clinkering in nature. Fluidised-bed combustion and direct ignition of pulverised coal technologies are already existing. Information on sliding pressure boilers, coal water fuels, magnetic hydrodynamics and thermal repowering make an interesting reading.

The Report gives a good comparison of drum type and once through boilers. In fact, report also gives a good deal of information on the use of Indian coals in boilers for power generation with some of the following recommendations and conclusions. The ash contents in Indian coals is high and is abrasive in nature. To counter this, adaption of single pass boilers (tower type boilers) after having necessary feedback from the present users, has been recommended. Direct ignition of pulverized coal (DIPC) results in substantial oil savings during startups and low load operation. Advanced technologies such as fluidized bed combustion and slagging combustor offer better efficiencies and versatility in utilizing different grades of coal. Research is being carried out in slagging combustors. Coal water fuels are basically used abroad for conversion of existing oil-fired boilers to coal firing. The coal fuel technology offers scope for utilizing the fines in coal beneficiation plants and also to reduce load on existing rail/road transport system by transporting the coal in a slurry form through pipes. The report describes that considering the future power generation programme in the country, collaborations appear necessary in the areas of super-critical pressure boilers and pressurised fluidized bed combustion boilers. Collaborations may also be necessary in the areas of bag-house filters and pollution control technology for limiting SO₂ emissions.

There is a need to: (1) supply uniform quality of coal to the various thermal power stations in the country, (2) install coal beneficiation plants after necessary techno-economic study, (3) utilize fines in coal beneficiation plants, (4) adapt sliding pressure technology, and (5) variable speed fan drives. Further feedback is necessary in the following technologies—once through boilers, single pass boilers, slagging combustor technology, etc. New collaborations with overseas manufacturers for the design and manufacture of high cap-

acity (750-800 MW) super-critical boilers, adaption of technology for burning a wide range of coals have been recommended.

The quality of coal available for thermal power stations in India is significantly poor. This results in problems like higher erosion on the heat transfer surfaces, milling system, pulverized fuel pipelines, increased combustion of supporting oil due to low volatile matter in coal, higher volumes of ash handled in ESP, etc. Several indigenous efforts like liberal sizing of furnaces and ESP, use of casette baffles to protect heat transfer surfaces in economiser, use of special material to prevent erosion in coal pipes and bends, use of split coal nozzles, use of opposed firing and downshot firing systems to reduce support oil consumption, use of proven reliable mills of longer life, etc. have been adapted to overcome problems in burning low grade coals.

Coal beneficiation would reduce the undesirable uncombustibles in the coal being received at site. This would reduce erosion effect particularly on the mill components resulting in improved availability of the unit.

The analysis of forced outages of various modifications done to various units will be very helpful to boiler operating managers. The report in a book form is an invaluable treatise on the total aspects of Indian high pressure boiler industry and this will be useful to fuel technologists and other readers.

Dr D K Sharma

Fuels and Biofuels Engineering Laboratory
Centre for Energy Studies
Indian Institute of Technology
New Delhi 110 016

New Projects for Small Entrepreneurs (Chemical Products) (Development Commissioner Small Scale Industries, Department of SSI & ARI, Ministry of Industry, Govt. of India, Nariman Bhawan, New Delhi 110 011), 1st Edn, Vol. I (1993) pp. 158, price Rs 47.00, £ 1.26m \$ 1.78

The Small Industries Development Organisation has been catering to the need of small entrepreneurs for identification of industrial opportunities in the country. The present volume is an outcome in the same stream. There are 40 project profiles of chemical products which offer the best opportunities to choose from for a prospecting entrepreneur. The profiles provide basic information and serve as a useful preliminary guide. These have been prepared in-house by technical experts serving in Small Industries Service Institutes spread all over India. The project profiles

give market potential of each chemical product discussed, its process of manufacture, machinery and raw materials required, quality control, capital requirement (both fixed and running), cost of production, profitability, break-even point, marketing strategy, equipment suppliers, and raw material suppliers. In the appendices are given the addresses of Small Industries Service Institute all over India who can be contacted for further help. Some of the important chemical projects are: Acid Slurry, Detergents, Anodising and Dyeing of Aluminium Articles, Ayurvedic Medical Formulations, Cashewnut Shell Liquid, Disposable Syringes, Drycell Batteries, ECG Paper, Mosquito Repellent Mats, Gold Plating Metallic Optical Frames, Chrome Plating, Plastic Moulded Luggage, Refining of Used Lubricating oil, Sachharine, Printing Ink, Sulphur Black Dye, Teflon Products and Zinc Plating on Iron.

TIFAC-CSIO Directory of Scientific Instruments and Components Manufacture in India (Central Scientific Instruments Organisation, Chandigarh), 1993, pp. 600. Price Rs 200.

The instruments industry in India has undergone a phenomenal growth over the last two decades or more. And the need for a reliable database on availability and indigenous manufacturing pattern of various types of scientific instruments in the country to serve as an encyclopaedic reference source cannot be over-emphasized. The Central Scientific Instruments Organisation (CSIO), Chandigarh, being a premier institution in the area, has attempted to create such a database. CSIO has been publishing since 1969, the reference document: Director of Scientific Instruments and Components Manufactured in India the second edition was brought out in 1977, third in 1985 and the latest one under the title TIFAC-CSIO Directory of Scientific Instruments & Components Manufactured in India, in 1993. The directory has been designed to meet the information requirements of a very wide spectrum of users, ranging from buyers of instruments to market researchers, entrepreneurs established a new ones planning to venture into the area, policy-makers and customs appraisers. All the editions have been well received and the success of this venture can be judged from the fact that the 1985 edition was recognized by the Government of India for self certification under Import Pass Book Scheme.

The present 1993 edition of the Directory is in four sections, covering:

Reference section—An overview of the indigenous instrument industry. Statewise geographical distribution of the industrial units, their sizes, employment

pattern, graphical presentation of manpower engaged in various categories of instrument industry; capital investment and sales analysis, etc.

Section A—A classified list of 3500 instruments and components with SITC (Standard International Trade Classification) and CCCN (Customs Cooperation Council Nomenclature).

Section B—Detailed information about instrument and component manufacturers along with their manufacturing programmes arranged statewise with alphabetical index in respect of manufacturing firms, their registered offices, works, branches, chief executives, agents, etc.

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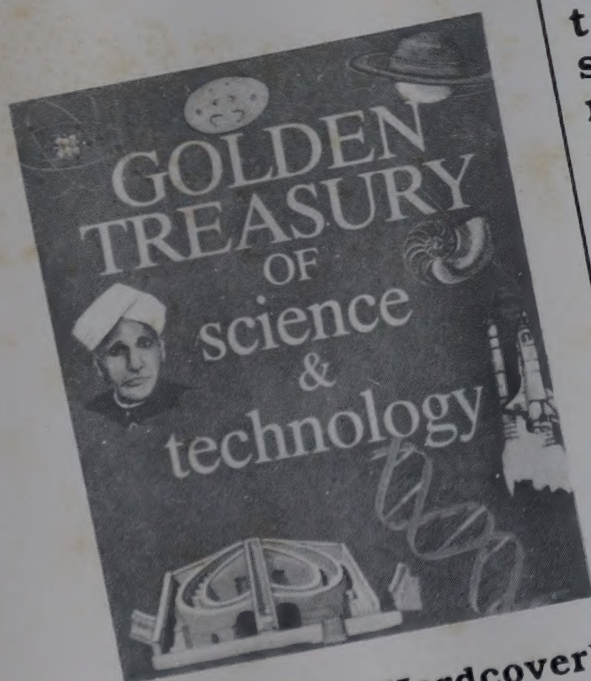
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